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THE ACTION OF WATER AND SALINE SOLUTIONS UPON CERTAIN SLIGHTLY SOLUBLE PHOSPHATES.[1]

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INTRODUCTION.

THE solubilities, so-called, of the slightly soluble phosphates have been frequently determined. The recorded data are, however, very conflicting and have little more than historical interest. The phosphates of iron, aluminum, and calcium are all substances which react with water, or are hydrolyzed, yielding, as one of the products of the reaction, phosphoric acid, which is much more soluble than the phosphate itself, and, at the same time, the hydroxide of the metal or possibly a basic phosphate, generally less soluble than the original phosphate. The solutions always contain free acid. It is not strictly correct, therefore, to speak of the solution, resulting from the action of water upon one of these phosphates, as a solution of the phosphate; rather it is a solution of the decomposition products, and the phosphate itself is, in many cases, present in negligible quantities only.

[1] Published by permission of the Secretary of Agriculture.

The relative masses of the solid phosphate and the solvent have a marked effect upon the amount of hydrolysis that takes place, and, therefore, upon the concentration of the resulting solution with respect to the phosphoric acid dissolved, owing, apparently, to the fact that the basic product of the hydrolysis has a marked effect in reducing the solubility or further hydrolysis of these phosphates. The extent of hydrolysis is markedly affected by the temperature. Finally, the reaction between the phosphates and water, at ordinary temperatures, is usually a rather slow one, final equilibrium conditions probably being approximated only after many days of contact. These facts have not been recognized or they have been generally ignored in work upon these phosphates, and consequently it will not be necessary to consider the earlier work except incidentally, as it bears upon details of this investigation.

The work recorded in the following pages has all been done with artificially prepared material. The investigation will be extended to include phosphates occurring in nature, as well as a number of other artificially prepared phosphates. For assistance in the experimental work, described in this paper, acknowledgment is due Dr. Atherton Seidell, who is continuing the investigation along certain lines, which will be described in a later communication.

EXPERIMENTAL METHODS.

In some of the experiments, the results of which are given in the following pages, large quantities of solution were used. In the majority of cases the procedure employed was to weigh the solid phosphate into a bottle and then add 200 cc. of water or solution. It is believed, however, that the relationships are more clearly seen by calculating the results to the basis of 1 gram of solid phosphate and varying amounts of solvent.[1] Eight-ounce sterilizer bottles, tightly closed with rubber stoppers, were found to be very convenient. The bottles were completely immersed in a constant temperature-bath which varied less than 1° C. during the experiment. In some cases the bottles were occasionally shaken by hand, but in others they were placed in a submerged

[1] That this procedure is justifiable was shown by two series, in one of which 2, 4 and 10 grams of iron phosphate were in contact with 40, 80 and 200 cc. of water, respectively for ten days, and in the second series double the amounts of phosphate were in contact with the same amounts of water. In both series the amount of PO_4 per liter dissolved and the acidity were found to be constant for the series within the limits of error of experimentation.

rotating cradle, driven by an electric motor, and the contents thus kept constantly agitated. When the solutions had remained in the constant temperature-bath the desired length of time, the bottles were placed in an upright position for twenty-four hours, or longer, to permit the suspended solid particles to subside, as far as possible, and then the supernatant solutions were passed through filters. An aliquot part of the clear filtrate, usually 100 cc., was then titrated with a standard solution of potassium hydroxide free from carbonates, using phenolphthaleïn as indicator, to determine the "acidity" of the solution. The results, when given, are always expressed as the number of cubic centimeters of tenth-normal potassium hydroxide solution required to neutralize a liter of the solution. The phosphoric acid was then precipitated, in the usual way, as phosphomolybdate, and estimated gravimetrically as magnesium pyrophosphate, or occasionally by titrating the yellow phosphomolybdate precipitate with a standard solution of alkali. In a few cases the dissolved phosphoric acid was present in such small quantities that it was found desirable to estimate it by a colorimetric method. In determining the phosphoric acid present in those solutions which also contained considerable amounts of potassium chloride, potassium sulphate or sodium nitrate, by precipitation as phosphomolybdate, it was important to see if the solubility of the phosphomolybdate precipitate was increased by the presence of the soluble salt to such a degree as to affect materially the results and necessitate a correction. To this end a solution of sodium phosphate was prepared, containing 0.0782 gram PO_4 per liter. To three separate portions potassium chloride, potassium sulphate and sodium nitrate, respectively, were added in the proportions of 75 grams per liter, and the solutions analyzed by the usual procedure. The results are given in Table I, from which it appears that any effect that the added salt may produce is within the usual error of manipulation.

TABLE I.—INFLUENCE OF ADDED SALTS ON THE PRECIPITATION OF THE PHOSPHOMOLYBDATE.

Salt added, 75 grams per liter.	PO_4 found, grams per liter.
.....	0.0782
KCl	0.0776
K_2SO_4	0.0784
$NaNO_3$	0.0778

The dissolved bases, whenever estimated, were determined in a separate aliquot part of the solution by standard methods.

IRON PHOSPHATE.

The phosphates of iron used in this work were precipitated by adding solutions of sodium hydrogen phosphate to solutions of ferric nitrate. Two products were prepared. In the preparation of one of these products the resulting supernatant solution, which is always acid, was carefully neutralized by the addition of sodium carbonate solution. Both precipitates were carefully washed a great number of times (about 100 times) by trituration and decantation with both hot and cold water until no traces of nitrates could be detected in the wash liquid by the phenoldisulphonic acid method. When thus prepared, both the products gave, with water, solutions more or less acid. The first product prepared in the slightly acid solution and designated as *iron phosphate* (A) showed a relative excess of phosphoric acid over that required by the formula $FePO_4$, while the second product, prepared by neutralizing with sodium carbonate and designated as *iron phosphate* (B), showed, on analysis, a percentage of iron greater than that required by the formula. Product (A) was perfectly white when first prepared, but later acquired a faint yellow tinge. The color of product (B) was white or pale yellow when first prepared and while yet moist, but on drying and standing it changed to a decided yellow.

The preparation of a product which would contain just the proportions of iron and phosphoric acid required by the formula $FePO_4$ is, of course, possible, though somewhat difficult.[1] A product containing an excess of the acid might be washed with successive portions of pure water until the residue had, on analysis, the desired composition. On the other hand, a product containing an excess of the base might be washed with successive portions of a solution of phosphoric acid. As the result of several experiments a curve could be readily constructed from which, by interpolation or extrapolation, the correct proportions of salts could be approximated, which would yield a precipitate of the desired composition. Other methods could undoubtedly be devised. From lack of attention to temperature and concentration condi-

[1] "Sur les phosphates de sesquioxyde de fer et d'alumine," by M. Millot, *Compt. Rend.*, **82**, 89 (1876).

tions the directions found in the literature for the preparation of this substance are generally unsatisfactory.

For this investigation it was not deemed worth while to attempt the preparation of a product of any particular composition, as the analytical results would be no criteria whatever as to the constitution of the amorphous product obtained, and no other satisfactory means to this end suggested themselves. Since, therefore, the product which must be employed is of an indefinite nature and the possibility of its exact reproduction a matter of doubt, it was considered more desirable to investigate two products of compositions on either side of that indicated by the formula $FePO_4$. The absolute value of the figures obtained for the solubility or decomposition of these iron phosphates have, at most, but a secondary interest. Their importance lies primarily in their comparative values and to show the order of magnitude which might be expected from products of analogous origin or composition.

The analysis of the iron phosphate was made with considerable difficulty, especially the iron determinations. The most satisfactory method was to reduce the iron and titrate with a standard solution of potassium permanganate, but, as others have found,[1] the reduction of the iron is accomplished with difficulty. The water contained in both products could not be accurately determined directly, since a constant weight could not be reached even at the highest temperature obtainable in a large combustion furnace.

Lachowicz[2] has published a very interesting paper on the behavior of ferric phosphate in the presence of water and saline solutions. He quotes a number of authorities as to the preparation of iron phosphate, himself investigates several methods, and concludes that a precipitate corresponding to the formula $FePO_4$ can only seldom be obtained. He gives the results of several authorities as to the solubility of iron phosphate in water, with and without dissolved carbon dioxide, and calls attention to the observations of Senft[3] that ammonium humate increases the solu-

[1] "On the Composition of Ferric Phosphate," by G. W. Waine, *Chemical News*, **36**, 132 (1877).

[2] *Monatsh. Chem.*, **13**, 357 (1892).

[3] Gesteins- und Boden-Kunde, 329 (1877). Senft's experiments, however, prove nothing conclusive as to the action of the humic acid, since his observations are easily accounted for by the free or hydrolyzed base necessarily present.

bility, to those of Luna[1] that the presence of potassium, sodium and ammonium salts also increases the solubility, and that of Kosbitscheff[2] that calcium carbonate, and especially the bicarbonate, increases the solubility. Lachowicz concluded from his experiments that although water *dissolves* very little iron phosphate it *decomposes* it to a considerable extent, and that the amount of the decomposition is dependent upon the relative masses of the phosphate and the water in contact with it. These conclusions are confirmed by the more elaborate experiments described in this paper. It was also shown by Lachowicz that the effect of water upon the phosphates was decreased by iron hydroxide. Saturating the water with carbon dioxide produced no appreciable effect in its action on the iron phosphate, an observation made also by Gerlach,[3] who found further that when calcium carbonate was mixed with either iron or aluminum phosphate in water that carbon dioxide caused an increased amount of calcium to go into solution without producing any noticeable effect upon the amount of dissolved phosphoric acid. A most interesting and suggestive set of experiments was performed by Lachowicz to show the influence of various salts in solution upon iron phosphate as compared with the action of pure water, but his conclusions in this matter cannot be accepted as more than suggestions for further experiments, since the solutions were in contact with the solid for only twenty-four hours, an entirely insufficient time for the true effects to become established. It appears, from Lachowicz's experiments, and is confirmed by this investigation, that the sulphates of the alkali metals increase the amount of phosphoric acid in the solutions as do salts which themselves hydrolyze with the formation of alkaline solutions, such as the carbonates or acetates of the alkalies. This action of hydrolyzed bases is most strikingly brought out in the case of disodium phosphate, which markedly increases the solubility of the iron phos-

[1] Heiden's "Lehrbuch der Düngungsmittel," 2nd Ed., p. 494. Luna's observations, however, are not confirmed by the work of Lachowicz or the present investigation.

[2] Sutherst (*Chem. News*, **85**, 157 (1902); *Agric. Gaz.* (London), **55**, 204 (1902)) found that lime increased the solubility of the phosphates of iron and aluminum, but thinks "it is essential that the lime should be in the form of hydrate, the carbonate being of no value whatever." H. J. Patterson (Penna. Dept. Agric. Bull. No. 94 (1902)) has made some very interesting observations on this subject from an agricultural point of view, from which it would appear that the solubility was increased by lime or the organic matter of soils. An opposite result, however, might have been expected from the research of Gerlach, cited in the text.

[3] *Landw. Versuchs-sta.*, **46**, 201 (1895).

phate, although, at first thought, a decreased solubility might be expected, due to the formation of a common ion. It is common knowledge that solutions of the alkali hydroxides will dissolve iron phosphates, as will also, though less readily, solutions of free mineral acids. Gerlach[1] found that oxalic acid was a more effective solvent than citric acid, which, in turn, was much more effective than acetic acid; in the presence of an excess of free iron hydroxide the solvent action of oxalic acid was unaffected, while that of citric acid was much lowered, and acetic acid did not dissolve enough phosphoric acid to be detected. Lachowicz studied the action of humic acid (?), but his experimental results hardly warrant his conclusion that this substance increases the solubility of iron phosphate, since the observed effects were more probably due to the free bases, also present in the solution, as a result of the hydrolysis of the supposed humates.[2] His experiments at 100° C. show, as might be expected, that temperature has a large influence on hydrolysis, but they are also unsatisfactory on account of the time element.

IRON PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER.

Iron Phosphate (A).—The average of a number of analyses of this product gave 51.26 per cent. PO_4, 27.20 per cent. Fe, corresponding to a mixture containing 73.31 per cent. $FePO_4$, with an excess of 5.15 per cent. PO_4.

TABLE II.—IRON PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER.

Temperature, 25° C.

	Grams PO_4 per liter of solution.			
Cc. water per gram of solid.	Series I. One minute shaking; twenty-four hours settling.	Series II. One day shaking; twenty-four hours settling.	Series III. Four days shaking; twenty-four hours settling.	Series IV. Seven days shaking; twenty-four hours settling.
10	0.214	0.267	0.286	0.320
50	0.086	0.107	0.118	0.142
200	0.027	0.041	0.047	0.056
800	0.010	0.013	0.016	0.020

Several series of experiments were made with this substance to obtain an idea as to how rapidly equilibrium would be ap-

[1] *Loc. cit.*

[2] See also the work of Schneider (*Ztschr. anorg. Chem.*, **5**, 84 (1894); **7**, 386 (1894)), who studied not only the action of ammoniacal solutions of humus upon iron phosphates, but also that of alkalies and carbonates. From his experiments it seems that the solubility of the phosphate is increased by ferric chloride or ferrous sulphate, probably on account of the free hydrolyzed acid which these salts yield.

proached when it was brought into contact with water at 25° C. The results obtained from four of these series are given in Table II, from which it appears that phosphoric acid was still going into solution in considerable amounts after seven days of contact, no matter what the proportion of water to solid might be. Two more series at this same temperature were then examined at intervals of twelve and forty-three days, the results being given in Tables III and IV.

TABLE III.—IRON PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER. Temperature, 25° C. Time of contact, twelve days, with frequent agitation.

Cc. water per gram of solid.	Gram PO_4 dissolved per liter.	Acidity.
5	0.512	78.0
10	0.391	60.4
20	0.283	48.2
33.3	0.215	34.0
40	0.189	33.4
60	0.152	26.9
80	0.120	21.9
100	0.107	19.4
200	0.070	12.8
400	0.042	8.0

TABLE IV.—IRON PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER. Temperature, 25° C. Time of contact, forty-three days, with constant agitation.

Cc. water per gram of solid.	Gram PO_4 dissolved per liter.	Acidity.
25	0.302	69.4
60	0.257	56.0
85	0.136	36.0
140	0.099	30.0
200	0.080	24.5
800	0.029	17.1

Some experimental evidence was obtained which indicated that phosphoric acid was still going into solution even after forty-three days contact with constant agitation of the mixture of solid and liquid. These tables show, however, the same general order of relative solubilities for different proportions of water to solid at the end of the several periods of time, and since the absolute value of the solubility figures for final equilibrium conditions are not of any special significance, and it was improbable that they would

bring out any relations not shown by the figures obtained within a convenient period of time, it was not deemed advisable to make further efforts to obtain final equilibrium conditions with this compound.

The figures given in the foregoing tables show conclusively that the greater the proportion of water in contact with iron phosphate the less was the concentration of the resulting solution with respect to phosphoric acid, although an easy and obvious calculation will show that the actual total amount which went into solutions increased with increased proportions of water.

In Tables III and IV are also given the acidity per liter of the solutions which also show that the larger the proportion of water to solid the less, relatively, was the decomposition, although actually it was greater. The titration figures themselves are given in these and the other tables in view of the lack of a satisfactory agreement with the gravimetric results. A calculation from the acidity figures, given in Tables III and IV of the equivalent amounts of phosphoric acid in the solutions, on the assumption that phosphoric acid is dibasic towards phenolphthaleïn, indicates, as do the figures determined gravimetrically, that an increasing proportion of solvent to solid phosphate takes into solution an actually increasing amount of phosphoric acid, yet *relatively* less is dissolved. The iron in the solutions, though its presence could in some cases be detected, contrary to the experience of Lachowicz, was not in sufficient quantities to admit of accurate estimation.

A series was determined also at 39° C., the results being given in Table V.

TABLE V.—IRON PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER.
Temperature, 39° C. Time of contact, sixteen days, with constant agitation.

Cc. water per gram of solid.	Gram PO_4 dissolved per liter.	Acidity.
50	0.267	42
200	0.109	18
1000	0.033	6

The gravimetric determinations show that the higher temperature tended to increase somewhat the extent of the reaction between the water and the iron phosphate, as might have been expected. This conclusion is apparently contradicted by the acidity

found, which is lower in the series run at the higher temperature, the significance of the acidity becoming thus even less explicable.

IRON PHOSPHATE (A) IN AQUEOUS SOLUTIONS OF SALTS.

Solutions of varying concentration with respect to sodium nitrate were put in contact with the iron phosphate, three different proportions of solution to solid being used. The results are given in Table VI.

TABLE VI.—IRON PHOSPHATE (A) IN SOLUTIONS OF SODIUM NITRATE.

Temperature, 25° C. Time of contact, forty days, with continuous agitation.

Grams $NaNO_3$ per liter.	Gram PO_4 dissolved per liter.	Acidity.
One gram solid per 20 cc. solution.		
0	0.3500	....
5	0.2237	73.2
25	0.1912	97.4
75	0.1622	118.4
150	0.1451	128.6
300	0.1084	130.6
One gram solid per 40 cc. solution.		
0	0.2175	....
5	0.1786	57.0
25	0.1558	74.0
75	0.1331	84.0
150	0.1124	88.0
300	0.0776	90.0
One gram solid per 100 cc. solution.		
0	0.1250	....
5	0.1130	33.0
25	0.0976	41.0
150	0.0615	50.0
300	0.0482	51.0

It will be seen that, no matter what the proportion of solution to solid may have been, with increasing concentration of sodium nitrate there was a decrease in the amount of phosphoric acid dissolved, but an increase in the acidity. So far no satisfactory explanation of these facts has been suggested.

In Table VII are given the results obtained by treating the iron phosphate (A) with solutions of potassium chloride. In

TABLE VII.—IRON PHOSPHATE (A) IN SOLUTIONS OF POTASSIUM CHLORIDE.

Temperature, 25° C.

Grams KCl per liter.	Gram PO_4 dissolved per liter.	Gram Fe dissolved per liter.	Acidity.
	One gram solid per 20 cc. solution		
0.0	0.3500	.....	....
0.111	0.2256	.....	57.6
0.272	0.2011	.....	59.4
0.444	0.1689	.....	64.9
5.0	0.1127	0.0429	119.6
25.0	0.0905	0.0480	174.2
75.0	0.0820	0.0540	209.2
150.0	0.0871	0.1020	224.0
300.0	0.0871	0.1420	234.0
	One gram solid per 40 cc. solution.		
0.0	0.2175	.....	....
5.0	0.09296	0.0152	84.0
25.0	0.07690	0.0168	114.0
75.0	0.05685	0.0200	128.0
150.0	0.05284	0.0320	139.0
300.0	0.04280	0.0700	141.0
	One gram solid per 100 cc. solution.		
0.0	0.1250	.....	....
5.0	0.0602	0 0128	44.0
25.0	0.0448	0.0144	58.0
75.0	0.0374	0.0168	66.0
150.0	0.0314	0.0248	68.0
300.0	0.0268	0.0376	69.0

these series, however, besides determining the amount of phosphoric acid and the acidity, the amount of iron in the solutions was also determined.

Here again it will be observed that with all the proportions of solution to solid phosphate an increasing concentration with respect to the potassium chloride was accompanied by a decrease in the concentration of dissolved phosphoric acid and an increase in the acidity; also the amount of iron dissolved increased. It would thus appear that the acidity of the solution was causally connected with the amount of iron dissolved, but in what manner is not clear, especially, as will presently appear, an opposite conclusion is indicated by the experiments with calcium phosphate. Calculating the acid equivalent of the iron found and adding the acid

equivalent of the phosphoric acid found on the assumption that both are trivalent, the sum does not account for the acidity actually found.

TABLE VIII.—SOLUBILITY OF IRON PHOSPHATE (A) IN SOLUTIONS OF POTASSIUM SULPHATE.

Temperature, 25° C. Time of contact, nineteen days.

Grams K_2SO_4 per liter.	Gram PO_4 dissolved per liter.	Acidity.
	One gram solid per 20 cc. solution.	
3	0.320	76.0
6	0.344	93.0
25	0.366	141.0
50	0.372	171.0
75	0.367	194.0
150	0.364	233.0

In Table VIII are given the results obtained in solutions of potassium sulphate, from which it will be seen that the presence of this salt somewhat increases the amount of phosphoric acid entering solution, thus confirming the conclusion of Lachowicz. The acidity of the solution is markedly increased with increasing amounts of the potassium sulphate.

IRON PHOSPHATE (B) IN VARYING PROPORTIONS OF WATER.

Iron Phosphate (B).—The results of a large number of fairly concordant analyses gave 44.33 per cent. PO_4 and 32.61 per cent. Fe, corresponding to a composition of 70.47 per cent. $FePO_4$, 12.37 per cent. $Fe(OH)_3$ and 17.16 per cent. H_2O.

This basic phosphate was treated with varying amounts of water, as already described under phosphate (A). No iron could be detected in the solutions and on account of the small amounts of phosphoric acid available for determination, the well-known colorimetric method was used.[1] The results are given in Table IX.

TABLE IX.—IRON PHOSPHATE (B) IN VARYING PROPORTIONS OF WATER.

Temperature, 25° C.

Cc. water per gram of solid.	Gram PO_4 per liter of solution.
66.6	0.072
100.0	0.061
200.0	0.037
400.0	0.033

[1] See West-Knights: *Analyst*, **3**, 197 (1880); Lepierre: *Bull. Soc. Chim.*, (3), **15**, 1213 (1896); Lepierre: *Ibid.*, (3), **25**, 800 (1901); Jolles and Neurath: *Monatsh. Chem.*, **19**, 5 (1898); Jolles: *Arch. f. Hygiene*, **34**, 22 (1899); Woodman and Cayvan: This Journal, **23**, 96 (1901); Woodman: *Ibid.*, **24**, 735 (1902); Veitch: *Ibid.*, **25**, 169 (1903); Schreiner: *Ibid.*, **25**, 1056 (1903).

It will be observed that the less the proportion of water to solid the greater is the concentration of phosphoric acid, but the actual amount dissolved from a given weight of solid becomes greater as the proportion of water increases. The solutions obtained were distinctly acid.

IRON PHOSPHATE (B) IN AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE.

TABLE X.—IRON PHOSPHATE (B) IN SOLUTIONS OF POTASSIUM CHLORIDE. Temperature, 25° C. Time of contact, fifteen days, with continuous shaking.

Grams KCl per liter.	Gram PO_4 per liter observed.	Gram PO_4 per liter corrected.[1]
One gram solid per 200 cc. solution.		
0	0.037	0.037
3	0.009	0.011
5	0.007	0.009
15	0.008	0.012

In Table X are shown the results obtained when the solid is kept in contact with solutions of varying concentrations with respect to potassium chloride. It will be observed that the potassium chloride enormously decreased the amount of PO_4 which went into solution, although Lachowicz found that practically no effect was produced by this salt, and the generalization of Luna[2] is also contradicted. The solutions in all cases were acid. Here also the amounts of phosphoric acid in solution were so small that it was found advisable to determine them by the colorimetric method. The figures given for the amounts of phosphoric acid in solutions, containing considerable quantities of

[1] The presence of considerable amounts of soluble salts influences the readings in the colorimetric determination of phosphoric acid; therefore Mr. J. G. Smith made some experiments on the subject. The influence of potassium chloride, in the concentrations used in the work described in the text, on the readings due to the phosphomolybdate coloration is shown in the following table:

Grams KCl per liter.	PO_4 parts per million of solution.			
0	5.0	10.0	15.0	20.0
3	4.7	8.0	12.3	15.8
5	4.6	8.2	10.9	13.7
15	4.0	7.2	10.1	12.5

It will be readily seen that increasing amounts of potassium chloride decrease the phosphomolybdate coloration, the effect being more marked in the higher concentrations with respect to phosphates. This effect is, however, small as compared with the enormous decrease produced by potassium chloride on the solubility of the iron phosphate as is shown when the results, given in the text as found, are corrected for the influence of the potassium chloride on the determination by interpolation from the results given in this table.

[2] *Loc. cit.*

potassium chloride, are not very satisfactory as to their absolute values, due unquestionably to errors of determination for such small quantities in the presence of relatively large quantities of other dissolved substances. The figures show, however, that even small quantities of potassium chloride greatly reduce the solubility of the phosphate as compared with the action of pure water, but that relatively large quantities of the potassium chloride produce but little more effect than do the smaller quantities.

ALUMINUM PHOSPHATE.

Aluminum phosphate was prepared in a similar way to that employed for iron phosphate. Three products were obtained: Aluminum phosphate (A) was prepared by adding dissolved sodium phosphate to a solution of aluminum sulphate and washing repeatedly with hot and cold water until the washings were free from sulphates. Aluminum phosphate (B) was prepared by adding a solution of ammonium phosphate to a solution of aluminum sulphate, partially neutralizing the supernatant acid solution with ammonium carbonate, decanting and washing the residue repeatedly until the presence of sulphate could no longer be detected in the washings. The residue still contained traces of ammonia, however, and the material was, therefore, strongly heated over the blast-lamp. Aluminum phosphate (C) was prepared by adding dissolved sodium phosphate to aluminum sulphate in the presence of sodium acetate.

There has been no work on the phosphates of aluminum, such as that of Lachowicz on the phosphates of iron, from which one might predict the action of water upon them, other than occasional observations that it behaved similarly to iron phosphate, but was less resistant than the latter to the action of water or saline solutions. The presence of carbon dioxide in the solution appears to have no appreciable effect upon the amounts of aluminum or phosphoric acid dissolved even when lime or magnesia is present.[1] The solubility is increased by the hydroxides of potassium or sodium, and to a lesser extent by free mineral acids. Gerlach found that oxalic and citric acids were about equally effective and much more so than acetic acid in bringing phosphoric acid into solution and that free aluminum hydroxide, while greatly re-

[1] Gerlach: *Loc. cit.*

ducing the action of the acetic acid, did not affect that of the oxalic or citric acids. Schneider[1] states that the solubility is increased by aluminum chloride or aluminum sulphate.

ALUMINUM PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER.

Aluminum Phosphate (**A**).--Analysis of the product showed it to contain 77.42 per cent. PO_4 and 21.49 per cent. Al, whereas the formula $AlPO_4$ requires 77.80 per cent. PO_4 and 22.20 per cent. Al. Two series with varying proportions of water were run at 25° C. for twenty-one days and forty-eight days respectively, the results obtained being given in Table XI.

TABLE XI.—ALUMINUM PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER.

Temperature, 25° C. Time of contact, twenty-one days, with continuous agitation.

Cc. water per gram of solid.	Gram PO_4 per liter.	Acidity.
25	0.6789	116.4
75	0.2477	45.2
175	0.1172	23.3
425	0.0589	13.0
800	0.0343	8.7

Time of contact, forty-eight days, with continuous agitation.

Cc. water per gram of solid.	Gram PO_4 per liter.	Gram Al per liter.	Acidity.
50	0.3886	0.0359	70.0
100	0.2110	0.0157	38.8
250	0.0968	0.0079	19.7
600	0.0516	0.0065	12.7
4000	0.0113	0.0033	4.2
8000	0.0049	.....	2.1

From these figures it will be seen that the phosphoric acid goes into solution quite slowly and that it is improbable that a final state of equilibrium was reached even after forty-eight days of contact. Both series show that while a greater amount of phosphoric acid goes into solution with the greater proportion of water to solid, the concentration of the resulting solution is less and the acidity also is less. The same statements would probably hold, moreover, for the aluminum, as shown in the figures obtained for the series carried forty-eight days.

[1] *Zischr. anorg. Chem.*, **5**, 87 (1894).

TABLE XII.—ALUMINUM PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER.

Temperature, 35° C. Time of contact, thirty days, with continuous agitation.

Cc. water per gram of solid.	Gram PO_4 dissolved per liter.
25	0.889
50	0.503
100	0.274
200	0.131

In Table XII are given the results obtained with aluminum phosphate (A) in contact with varying proportions of water at 35° C., which show that the reaction between the phosphates goes either farther or more rapidly at the higher temperature.

ALUMINUM PHOSPHATE (A) IN AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE.

TABLE XIII.—ALUMINUM PHOSPHATE (A) IN SOLUTIONS OF POTASSIUM CHLORIDE.

Temperature, 30° C. Time of contact, thirty days, with continuous shaking.

Grams KCl per liter of solution.	Gram PO_4 dissolved per liter of solution.
One gram solid per 100 cc. solution.	
0	0.287
5	0.270
35	0.266
125	0.249

In Table XIII are given results obtained with the phosphate in contact with solutions of varying concentrations in potassium chloride. The results show that as in the case of the iron phosphates, in the presence of increasing amounts of potassium chloride the amount of phosphoric acid going into solution is steadily decreased.

ALUMINUM PHOSPHATE (B) IN VARYING PROPORTIONS OF WATER.

Aluminum Phosphate (B).—The analysis of the substance gave 81.33 per cent. PO_4 and 21.16 per cent. Al.

In Table XIV are given the results obtained with the phosphate in contact with several proportions of water. With this product, also, the larger the proportion of water to solid the greater the actual amount dissolved, but the less the concentration of the resulting solution. The results, however, show that the product is much

TABLE XIV.—ALUMINUM PHOSPHATE (B) IN VARYING PROPORTIONS OF WATER.

Temperature, 30° C. Time of contact, thirty-five days, with continuous agitation.

Cc. water per gram of solid.	Gram PO_4 dissolved per liter.
20	0.241
40	0.134
80	0.081

less acted upon by the water than aluminum phosphate (A), and it seems probable that this fact is to be ascribed to some change produced by the heating before the blast-lamp, since it is not to be accounted for by a comparison of the analyses of the two substances.

ALUMINUM PHOSPHATE (B) IN AQUEOUS SOLUTIONS OF SALTS.

TABLE XV.—ALUMINUM PHOSPHATE (B) IN SOLUTIONS OF POTASSIUM CHLORIDE.

Temperature, 27° C. Time of contact, fifteen days, with continuous agitation.

Grams KCl per liter.	Gram PO_4 per liter.
One gram solid per 20 cc. solution.	
0	0.241
150	0.201
200	0.189
250	0.186
One gram solid per 80 cc. solution.	
0.0	0.081
2.5	0.071
17.2	0.067
60.9	0.065

In Table XV are given results which show that increasing amounts of potassium chloride decrease the amount of phosphoric acid going into solution, as was the case with aluminum phosphate (A), and the phosphates of iron.

TABLE XVI.—ALUMINUM PHOSPHATE (B) IN SOLUTIONS OF POTASSIUM SULPHATE.

Temperature, 35° C. Time of contact, ten days, with continuous agitation.

Grams K_2SO_4 per liter.	Gram PO_4 per liter.
One gram solid per 20 cc. solution.	
0.0	0.241
5.4	0.218
49.0	0.191
101.4	0.183

Grams K_2SO_4 per liter.	Gram PO_4 per liter.
One gram solid per 80 cc. solution.	
0.0	0.080
2.5	0.071
7.7	0.068
27.2	0.064
62.5	0.062

Table XVI shows that potassium sulphate, like potassium chloride, reduces or retards the reaction between the water and the solid phosphate. There is in this respect a notable difference between the phosphates of iron and aluminum.

TABLE XVII.—ALUMINUM PHOSPHATE (B) IN SOLUTIONS OF SODIUM NITRATE.

Temperature, 27° C. Time of contact, fifteen days, with continuous agitation.

Grams $NaNO_3$ per liter.	Gram PO_4 per liter.
One gram solid per 20 cc. solution.	
0	0.3094
20	0.2988
60	0.2818
140	0.2732
240	0.2220
One gram solid per 80 cc. solution.	
0.0	0.0811
2.5	0.0807
7.5	0.0798
17.5	0.0794
27.5	0.0790
87.5	0.0657

The results obtained with solutions of varying concentrations in sodium nitrate are given in Table XVII, and clearly show that the general effect of this salt is the same as that produced by the other salts studied.

ALUMINUM PHOSPHATE (C) IN VARYING PROPORTIONS OF WATER.

This product, on analysis, gave, from two closely agreeing sets of determinations, 48.79 per cent. PO_4 and 19.82 per cent. Al, showing an excess of aluminum over that required by the phosphoric acid found.

The results obtained with this basic phosphate in varying proportions of water are given in Table XVIII. The amount of phosphoric acid in the solution was so small that the colorimetric method had to be used.

TABLE XVIII.—ALUMINUM PHOSPHATE (C) IN VARYING PROPORTIONS OF WATER.

Temperature, 25° C. Time of contact, fifteen days, with constant agitation.

Cc. of water per gram of solid.	Gram PO_4 per liter.
66.66	0.0039
100.00	0.0037
200.00	0.0035
400.00	0.0039

ALUMINUM PHOSPHATE (C) IN AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE.

TABLE XIX.—ALUMINUM PHOSPHATE (C) IN SOLUTIONS OF POTASSIUM CHLORIDE.

Temperature, 25° C. Time of contact, fifteen days, with continuous agitation.

Grams KCl per liter.	Gram PO_4 per liter found.	Gram PO_4 per liter corrected.
One gram solid per 200 cc. solution.		
0	0.0035	0.0035
5	0.0028	0.0031
15	0.0027	0.0033

The results obtained with two concentrations of potassium chloride are given in Table XIX. These small amounts were determined colorimetrically, making the corrections for the influence of the potassium chloride on the coloration, as was done with the iron phosphate. The hydrolysis of the phosphate in water itself is already so slight that the effect of the potassium chloride is scarcely perceptible.

CALCIUM PHOSPHATE.

The preparation of a calcium phosphate, approximating to the formula $Ca_3(PO_4)_2$, is much more readily accomplished than in the case of the phosphate of iron or aluminum. Nevertheless, the product usually obtained, when the attempt is made to prepare the substance by precipitation, seldom corresponds to this formula, but may contain either a smaller or a larger proportion of the base than desired. The "solubility" of the phosphate, as given by different authorities, varies widely. It is dependent on the proportion of base present, whether freshly precipitated, dried or

ignited, whether a natural product, as an apatite, a phosphate rock, bones, etc., as witness the values obtained by Völcker,[1] Warrington,[2] Pollacci,[3] Reichardt,[4] Berthelot[5] and Longuinine,[6] Maly and Donath,[7] Jaffre,[8] Williams,[9] and others. The effect of various acids in increasing the solubility has been studied by Bischof,[10] Crum,[11] and many later investigators, mainly from the point of view of fertilizer analyses. For instance, Paturel[12] found that acetic acid, the presence of which in certain soils was proved, has a relatively greater solvent action than has citric acid. Causse[13] found that the presence of phosphoric acid increases the solubility of either tri- or dicalcium phosphate, the monocalcium salt being formed at ordinary temperatures, but some dicalcium phosphate separating from solutions which were first heated and then re-cooled. Sulphurous acid, according to Gerland,[14] also increases the solubility of tricalcium phosphate. Humic acid, according to Minssen and Jacke,[15] increases the solubility. The presence of calcium carbonate,[16] or calcium sulphate,[17] appears to depress the solubility, while ammonium salts[18] generally increase it, as do some other alkaline salts. That a rise in temperature or the presence of carbon dioxide[19] increases the solubility has been fre-

[1] Report British Assoc. Advancement of Science, 1862, 169; *Jsb. d. Chem.*, **131**, (1862).

[2] *J. Chem. Soc.*, **19**, 296 (1866); *Ibid.*, **24**, 80 (1871); *Ibid.*, **25**, 269 (1871); *Ibid.*, **26**, 983 (1873).

[3] *L'Oros*, **19**, 217 (1896); See Abstr., *J. Chem. Soc.*, **72**, ii, 260 (1897).

[4] *Ztschr. anal. Chem.*, **11**, 275 (1872).

[5] *Ann. chim. phys.*, [6], **11**, 350 (1887).

[6] *Ibid.*, [5], **9**, 33 (1876).

[7] *J. prakt. Chem.* [2], **7**, 413 (1873).

[8] *Bull. Soc. Chim.* [3], **19**, 372 (1898).

[9] *Chem. News*, **24**, 306 (1871).

[10] *J. prakt. Chem.* **67**, 39 (1833).

[11] *Ann. Chem.* (Liebig), **63**, 284 (1847).

[12] *Ann. Agron.*, **20**, 332 (1894).

[13] *Compt. Rend.*, **114**, 414 (1892).

[14] *J. prakt. Chem.* [2], **4**, 97 (1871).

[15] *Bied. Centrbl.*, **29**, 447 (1900).

[16] Warrington: *Loc. cit.*; Pollacci: *Loc. cit.*

[17] *Ann. Chem.* (Liebig), **198**, 290 (1879); Armsby: *Am. J. Sci.* [3], **12**, 46 (1876).

[18] Warrington: *Loc. cit.*; Ferreil: *Bull. Soc. Chim.* [2], **35**, 548 (1881).

[19] This observation, which was made in 1846 by Dumas (*Compt. Rend.*, **23**, 1018 (1846)) and by Lassaigne (*Compt. Rend.*, **23**, 1019 (1846); *J. Pharm.*, [3], **3**, 11 (1847); **5**, 258 (1849)) and practically every one who has worked with phosphates since, was confirmed in the course of the present investigation. It is remarkable because it might be expected that the increased solubility of the calcium induced by the presence of carbon dioxide would reduce the amount of phosphoric acid entering the solution, in view of the decrease observed in the presence of other calcium salts. Barillé (*Report Pharm.*, 1901, p. 145), who studied the action of carbon dioxide on solutions of tricalcium phosphate at increased pressures, reports that the biphosphate and calcium bicarbonate were formed, but that the bicarbonate decreased the solubility of the biphosphate.

quently observed, citations being too numerous to be given. Practically all observers have noted that the solutions of this substance were always acid and many have pointed out that the solid residue contains more base than before contact with water. It has been shown that when monocalcium phosphate or dicalcium phosphate is dissolved in water, dicalcium phosphate (or the hydrate $CaHPO_4.2H_2O$) may separate, leaving free acid as well as some calcium salt in the solution, but on boiling the solution and removing, in part, the acid, either by neutralizing or by decanting and using renewed portions of water, the residue is converted into tricalcium phosphate, or into a mixture with an even greater proportion of base.[1]

From these facts it appears that no matter what compound, or mixture of compounds, containing only calcium and phosphoric acid ($Ca_n(PO_4)_m$), be placed in water, there will result free phosphoric acid in the solution with separation of calcium hydroxide. The calcium hydroxide may then react to form a more basic and less soluble phosphate, or simply form a mixture with the phosphate, the solubility of which is decreased by its presence. The system is more interesting and more complex than the corresponding ones for iron and aluminum, respectively, owing to the existence, under certain concentration-temperature conditions, of the definite molecular species, mono-, di-, tricalcium phosphates (or hydrates of them) as solid phases in contact with the solution.[2]

[1] Joly: *Compt. Rend.*, **94**, 529 (1882); **97**, 1480 (1883); Joly and Sorel: *Ibid.*, **118**, 738 (1894); Barillé: *Report Pharm.*, 1897, p. 529; *Chem. Centrbl.*, I, **69**, 434 (1898); Viard: *Compt. Rend.*, **127**, 178 (1898); Delattre: *Bull. Soc. Chim.* (2), **35**, 358 (1881); Millot: *Ibid.* (2), **33**, 194 (1880); Wibel: *J. prakt. Chem.* (2), **9**, 113 (1874); Aeby: *Ibid.* (2), **9**, 469 (1874); Stoklasa: *Landw. Versuchs-sta.*, **38**, 401 (1891); **44**, 437 (1894); Rindell: *Compt. Rend.*, **134**, 112 (1902); *et. al.*

[2] From an agricultural point of view the above considerations have a special interest. They show that the process of "inversion" of phosphates in the soil to less soluble forms is but a process of hydrolysis, and that no matter what phosphate be put upon the soil the resulting phenomena are essentially the same; phosphoric acid will be continually given off to the soil solution, but in constantly decreasing amounts, or what is perhaps a more useful way to regard it, at a constantly decreasing rate. With any given soil, however, a number of factors enter which affect the rate of solution of the phosphoric acid, so that Schloesing (see excellent memoir of Paturel: *Ann. Agron.*, **28**, 385 (1902)) has suggested that the amount of water-soluble phosphoric acid in a soil is a constant definite characteristic (see also Bull. No. 22, Bureau of Soils, U. S. Dept. of Agr.). It would depend upon the lime and magnesia in the soil (Schloesing: *Compt. Rend.*, **127**, 236, 327 (1898); **131**, 149, 211 (1900); Jacobson: *Ann. Agron.*, **24**, 292 (1898); Schreiber: Expt. Sta. Rec., **7**, 104 (1895); Stahl-Schröeder: Expt. Sta. Rec., **4**, 587 (1893); Crawley: This Journal, **24**, 1114 (1902)); upon the iron and alumina in the soil (Georgievics: *Monatsh. Chem.*, **12**, 566 (1891)); upon the humus content (Dumont: *Compt. Rend.*, **132**, 435 (1901)); upon the absorptive power of the soil grains (Gerlach: *Landw. Versuch-sta.*, **46**, 201 (1895)); upon the presence of various soluble salts, etc., and probably the nature of the vegetation.

A number of the systems which these substances form with water are now under investigation in the laboratory. The following experiments were made with a specimen of precipitated calcium phosphate obtained from Eimer & Amend, and, on analysis, this product gave figures agreeing very closely with the formula $Ca_3(PO_4)_2$.

TABLE XX.—CALCIUM PHOSPHATE, $Ca_3(PO_4)_2$, IN WATER AFTER VARYING PERIODS OF CONTACT.

Temperature, 25° C. Constant shaking.

Number of days contact.	Gram PO_4 per liter.
One gram solid per 40 cc. solvent.	
1	0.1989
3	0.2060
8	0.2163
20	0.2288
37	0.2302
81	0.2339

In Table XX are given the results obtained by shaking the phosphate continuously in water at 25° C. for periods varying from one day to eighty-one days. It will be seen that the phosphate hydrolyzed at a constantly diminishing rate. A chart of these results would indicate that equilibrium was practically reached in about thirty-five days, although a small amount of phosphoric acid continued to go into solution, and it is improbable that complete equilibrium was established at eighty-one days. No especial significance can be attached to the absolute values of such figures, since the rate of solution would depend upon so many factors, fineness of the solid particles, vigor of shaking, temperature of solution when first prepared, etc., but the figures are of importance in showing that a very considerable length of time is required to bring about even an approach to equilibrium conditions. In the experiments, the results of which are given in the following tables, the phosphate was left in contact with the solvent for varying lengths of time, until it was believed that equilibrium conditions were approximated sufficiently near to establish the true character of the results sought, and justify their use for comparative purposes. It seems worth while to emphasize here that such comparative figures alone have any significance

when dealing with a substance of the indefinite character possessed by the phosphate with which this work was done. That is, when working with a substance whose composition alone is known, as shown by analysis, but whose constitution, whether it be one distinct molecular species or a mixture, is uncertain. It seems well, moreover, to repeat that the true solubility of the substance is probably very small, practically indeterminate with our present facilities and of but little interest, and that it is the solutions of the hydrolyzed or decomposition products with which one has to deal. Unless a perfectly definite molecular species be under consideration, there is nothing to be gained by waiting for final equilibrium to become established so long as it is clearly understood that considerable lengths of time are required for complete equilibrium, and that the figures obtained are for comparative purposes only.

CALCIUM PHOSPHATE IN VARYING PROPORTIONS OF WATER.

TABLE XXI.—CALCIUM PHOSPHATE, $Ca_3(PO_4)_2$, IN WATER FREE FROM CARBON DIOXIDE.

Temperature, 25° C. Time of contact, twelve days, frequent shaking.

Cc. of water per gram of solid.	Gram PO_4 per liter of solution.
2.5	1.2293
5.0	0.9049
10.0	0.6805
20.0	0.3825
40.0	0.2156
60.0	0.1668
80.0	0.1315
100.0	0.1131
200.0	0.0679
400.0	0.0427

In Table XXI are given the results obtained from a series of solutions obtained from calcium phosphate in contact with varying proportions of water. It will be observed that here, as in the similar experiments with the phosphates of iron and aluminum, that while the actual amount of phosphoric acid dissolved increases as the proportion of water to solvent increases, the relative concentration of the solution decreases.

CALCIUM PHOSPHATE IN AQUEOUS SOLUTIONS OF SALTS.

In Tables XXII and XXIII are given the results obtained with

TABLE XXII.—CALCIUM PHOSPHATE, $Ca_3(PO_4)_2$, IN SOLUTIONS OF CALCIUM CHLORIDE WHEN IN THE PROPORTION OF 1 GRAM CALCIUM PHOSPHATE TO 40 CC. SOLUTION.

Temperature, 25° C. Time of contact, five days, with continuous shaking; one day settling.

Grams $CaCl_2$ per liter.	Gram PO_4 dissolved per liter.
0	0.2185
1	0.1383
5	0.1150
10	0.1050
25	0.0979
50	0.0905
100	0.0797
200	0.0626

TABLE XXIII.—CALCIUM PHOSPHATE, $Ca_3(PO_4)_2$, IN SOLUTIONS OF CALCIUM CHLORIDE, WHEN IN THE PROPORTION OF 1 GRAM CALCIUM PHOSPHATE TO 100 CC. SOLUTION.

Temperature, 25° C. Time of contact, fifteen days, frequent shaking.

Grams $CaCl_2$ per liter.	Gram PO_4 dissolved per liter.
2.50	0.0684
5.00	0.0604
6.25	0.0600
12.50	0.0548
25.00	0.0511
50.00	0.0502

solutions of calcium chloride, from which it appears that increasing the concentration with respect to the latter salt decreases the amount of phosphoric acid entering the solution.[1]

This effect may possibly be ascribed to the formation of a common ion (Ca^{++}) from both substances, and a "forcing back" of the solubility of the calcium phosphate or hydrolyzed calcium hydroxide, and in consequence a lessening of the amount of phosphoric acid entering the solution. The same explanation suggests itself for the results given in Table XXIV, showing that increasing amounts of calcium nitrate also decrease the amount of the

[1] The following figures obtained in the course of another investigation, in which N/200 hydrochloric acid was used instead of pure water, may be of interest in this connection. The results show that in the dilute acid, although the absolute solubility is greater, the depressing influence of the calcium chloride is nevertheless quite marked.

CALCIUM PHOSPHATE, $Ca_3(PO_4)_2$, IN N/200 HYDROCHLORIC ACID CONTAINING CALCIUM CHLORIDE WHEN IN THE PROPORTION OF 1 GRAM CALCIUM PHOSPHATE TO 40 CC. SOLUTION.

Temperature, 25° C. Time of contact, five days, with continuous shaking; one day settling.

Grams $CaCl_2$ per liter.	Gram PO_4 dissolved per liter.
0.00	0.3154
1.00	0.2745
5.00	0.2527
10.00	0.2455
25.00	0.2254
50.00	0.2125
100.00	0.1878
200.00	0.1421

TABLE XXIV.—CALCIUM PHOSPHATE, $Ca(PO_4)_2$, IN SOLUTIONS OF CALCIUM NITRATE.

Temperature, 25° C. Time of contact, sixteen days, with constant shaking.

Grams $Ca(NO_3)_2$ per liter.	Gram PO_4 per liter.
One gram solid to 40 cc. solution.	
0.0	0.2163
1.0	0.1907
5.0	0.1110
10.0	0.1053
25.0	0.1064
50.0	0.1098
100.0	0.1132
200.0	0.1093
One gram solid to 100 cc. solution.	
2.5	0.0598
5.0	0.0452
6.25	0.0404
12.50	0.0223
25.00	0.0045
50.00	trace

phosphoric acid entering the solutions.[1] That calcium sulphate[2] and calcium carbonate[3] have a similar depressing effect has already been noted.

The same line of argument, however, does not appear satisfactory when potassium chloride is used. It might be expected that this salt would increase the solubility of the calcium phosphate and thus increase the amount of phosphoric acid entering the solution. But Table XXV shows a contrary effect. The acidity of the solution is also decreased with increasing concentration with respect to the more soluble salt, but the amount of calcium increases. The effect may be due to the increase in the solubility of calcium hydroxide produced by the potassium chloride, although, as shown by Cabot,[4] the solubility curve for this pair of electrolytes passes through a maximum point and the solubility of calcium hydroxide is actually less, when upwards of 200 grams of potassium chloride per liter are present, than in pure water. Therefore, when formed by the action of the water on the calcium phosphate, calcium hydroxide does not so com-

[1] The acidity of the solutions, however, increased.

[2] *Ann. Chem.* (Liebig), **198**, 290 (1879) : Armsby : *Loc. cit.*

[3] Warrington : *Loc. cit.*

[4] *J. Soc. Chem. Ind.*, **16**, 417 (1897).

TABLE XXV.—CALCIUM PHOSPHATE, $Ca_3(PO_4)_2$, IN SOLUTIONS OF POTASSIUM CHLORIDE.

Temperature, 25° C. Time of contact, thirty days, with frequent shaking.

Grams KCl per liter.	Grams PO_4 per liter.	Grams Ca per liter.	Acidity.
	One gram solid to 20 cc. solution.		
5	0.3278	0.0357	28.0
25	0.3227	0.0829	27.4
75	0.3193	0.1129	23.6
150	0.2971	0.1286	21.8
300	0.2356	0.1329	17.8
	One gram solid to 40 cc. solution.		
5	0.2265	0.0329	17.0
25	0.2224	0.0614	15.0
75	0.2157	0.0672	13.0
150	0.2151	0.0757	11.0
300	0.2137	0.0800	10.0
	One gram solid to 100 cc. solution.		
5	0.1280	0.0286	12.0
25	0.1273	0.0329	6.0
75	0.1240	0.0457	4.5
150	0.1126	0.0400	4.0
300	0.1032	0.0415	4.0

pletely separate from the solution if potasssium chloride be present, and the depressing action on the solubility of the phosphoric acid which might normally be expected from the hydroxide is shown.

While with increasing concentration of the solution with respect to potassium chloride calcium phosphate is like iron or aluminum phosphate in yielding a decreasing amount of phosphoric acid, and an increasing amount of the base, the calcium salt is different from those of iron and aluminum in that the acidity decreases instead of increases. With sodium nitrate in the solutions the results obtained and given here in Table XXVI were not very satisfactory. The gravimetric determinations of the phosphoric acid found in the solutions indicate that the nitrate has very little effect upon the amount entering solution. The titration figures, however, indicate that the solubility is decreased by the presence of the nitrate, differing in this respect from the results obtained in the case of iron phosphate. But the amount of calcium which enters the solution is markedly increased by the addition of sodium nitrate to the solution.

TABLE XXVI.—CALCIUM PHOSPHATE, $Ca_3(PO_4)_2$, IN SOLUTIONS OF SODIUM NITRATE.

Temperature, 25° C. Time of contact, thirty days, with frequent shaking.

Grams $NaNO_3$ per liter.	Gram PO_4 per liiter.	Gram Ca per liter.	Acidity.
	One gram solid to 20 cc. solution.		
5	0.3073	0.0643	27.8
25	0.2971	0.1572	26.0
75	0.3244	0.1958	24.6
150	0.3142	0.3901	22.8
300	0.3190	0.5916	20.6
	One gram solid to 40 cc. solution.		
5	0.1889	0.0329	18.0
25	0.2291	0.0757	16.0
75	0.2372	0.1057	14.5
150	0.2425	0.1343	13.0
300	0.2077	0.1315	11.0
	One gram solid to 100 cc. solution.		
5	0.1313	0.0272	8.0
25	0.1300	0.0486	7.0
75	0.1313	0.0600	6.5
150	0.1394	0.0729	6.0
300	0.1404	0.0843	5.0

SUMMARY.

From the foregoing description it appears that the rate of action of water upon phosphates of iron and aluminum, or upon tricalcium phosphate is very slow, so that neither in this investigation nor, probably, in any yet recorded, have final equilibrium conditions been observed. Free acid accumulates in the solution and a portion of the corresponding base is precipitated. While the free phosphoric acid tends to increase the solubility of the phosphate, the base, even though in solution in correspondingly smaller amounts, exerts a greater effect in decreasing it. Therefore, the addition of increasing amounts of water produces a relatively smaller (though in actual amounts a larger) solution and decomposition of the phosphate. This view is substantiated by the decreased effect observed with calcium phosphate, when calcium chloride or nitrate is present in the solution, but is apparently negatived by the increased action of soluble iron salts on iron phosphate and aluminum salts on aluminum phosphate observed by Schneider, although, as these readily soluble salts are them-

selves greatly hydrolyzed with the formation of free acids, it is probable that the effects observed upon the phosphates are due to these free acids.

The relatively decreasing effect of increasing amounts of water may, in part at least, be due to the differences in size[1] of the particles composing the solid phosphate. If there were material differences in the size of the particles and the smaller particles should dissolve or decompose more completely or more rapidly, then, as was observed, the solutions in contact with the larger proportion of water would be the more concentrated. Adsorption phenomena also may very probably play some part in these results, but, if proportional to the concentration of the supernatant solution, they should be in the opposite direction to the results observed.

The presence of potassium chloride in the solution decreases the amount of phosphoric acid obtained from iron, aluminum or calcium phosphate. It increases the amount of iron, aluminum or calcium entering the solution, although so few determinations were made in the case of aluminum that it has not been deemed worth while to give them here.

Potassium sulphate, as previously observed by Lachowicz, increases the amount of phosphoric acid entering the solution from iron phosphate, but decreases the amount entering the solution from aluminum phosphate.

Sodium nitrate decreases the amount of phosphoric acid entering the solution from either iron or aluminum phosphate, but appears to slightly increase the amount yielded by calcium phosphate, while it greatly increases the amount of calcium yielded to the solution by the last-named substance.

The acidity figures given in the foregoing pages are approximations only, since any experimental error in the determination is multiplied at least ten times. The titration of phosphoric acid is not very satisfactory and in the cases of solutions with rather high concentrations of soluble salts is distinctly unsatisfactory. Nevertheless, the figures given are believed to be sufficiently near the true values to warrant publication and to bring out the existing relations. With pure water in contact with the phosphates the acidity of the resulting solutions appears to be in

[1] See Ostwald : *Ztschr. phys. Chem.*, **34**, 495 (1900), and Hulett : *Ibid.*, **37**, 385 (1901).

the same direction as the concentration with respect to phosphoric acid, but no satisfactory correlation has been made between the two sets of determinations. In solutions of more soluble salts in contact with the phosphates, no generalization whatever seems justified. Potassium chloride, potassium sulphate and sodium nitrate all increase the acidity of solutions in contact with iron phosphate, while potassium chloride and sodium nitrate decrease the amount of the phosphoric acid in the solution. No correlation of the acidity with the amounts of iron in the solution seems possible, although, as is shown by the solutions of potassium chloride, the base in solution is increased.

In contact with calcium phosphate, potassium chloride and sodium nitrate decreased the acidity of the solution instead of increasing it, as in the case of iron phosphate. In both cases, however, the amounts of calcium in the solutions decidedly increased, and in the case of sodium nitrate the phosphoric acid also.

In so far as observations were made, an increase of temperature increased the decomposition of the solid phosphates in either water or salt solutions.

Owing to the complexity of the reactions involved between the hydrolyzed products and the other solutes, and perhaps also to the fact that definite equilibrium conditions were not under observation, attempts to apply the mass law to the results have not been satisfactory. The hypothesis of electrolytic dissociation has, in many of the cases observed, failed to give a satisfactory explanation.

The importance of the phenomena here described for agricultural and mineralogical studies is obvious. Its discussion will, however, be given at a later stage of the study.

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A MODIFICATION OF THE FREEZING-POINT METHOD.

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THE usual method of determining molecular weights by measuring the lowering of the freezing-point depends upon slightly supercooling the solution and then allowing ice to form. This is

accompanied by a rise in temperature, and the highest reading which the thermometer shows is taken as the melting-point of the solution. Thus equilibrium between ice and solution is always reached with ascending temperature and by separation of ice.

It is theoretically possible to obtain the same temperature reading, however, in an entirely different way. If a solution be thoroughly stirred in contact with ice the ice will continue to melt and cool the solution even after the solution has reached the melting-point of the pure solvent, and the lowest temperature attainable by stirring a solution with ice will be the melting-point of the solution. The equilibrium will be the same whether it is reached with melting ice or with freezing ice.

Some time after we had begun the investigation of which this paper is a preliminary report,[1] there appeared a description of a very simple method for molecular weight determination, based upon this principle,[2] and which can be readily applied in all cases where the strength of the solution is readily obtainable by direct analysis. The method upon which we have been working, while based upon the same general principle, is, nevertheless, carried out by very different mechanical methods, and avoids the necessity for an analysis of the solution in all cases. In fact, the method is almost the exact counterpart of the Landsberger method as applied to boiling-point determination. In the Landsberger method vapor is passed into the solution until the maximum temperature is reached, and the composition of the solution is determined by weighing both the dissolved substance and the total solution.

DESCRIPTION OF THE METHOD.

Briefly described, our method consists in the preparation of a stirrer of ice, by means of which first the pure solvent is thoroughly agitated and the thermometer reading taken in order to know the melting-point of the pure solvent. Next a quantity of the substance whose molecular weight is to be determined is added and brought into solution by shaking. The solution thus obtained is then thoroughly stirred with the ice-stirrer and the melting-point of the solution is found.

In order to obtain the concentration of the solution the tube in which the determinations were made was first weighed empty,

[1] The publication is made on account of the departure of Mr. Sloan from this laboratory.

[2] Richards: *Ztschr. phys. Chem.*, **44**, 563; This Journal, **25**, 291.

then, after a determination had been made, the total weight was again determined. Subtracting from the total weight the weight of the tube and of the dissolved substance the weight of the solvent is obtained, and thus all the data necessary for the computation of the molecular weight.

THE APPARATUS.

(1) *The Tube.*—The first determinations were carried out in the ordinary Beckmann apparatus, but as the results obtained

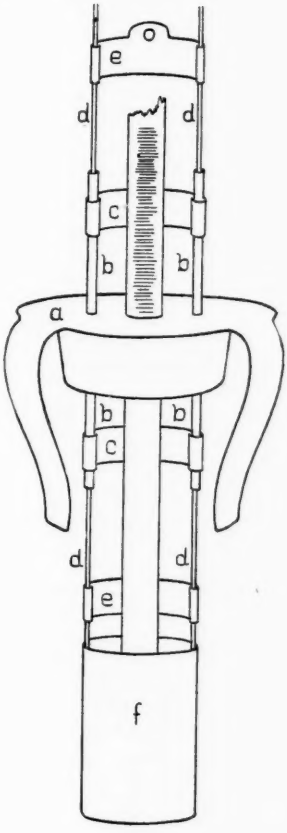

Fig. 1.

showed very considerable fluctuations, recourse was finally had to a vacuum jacket whereby the rate of radiation was very materially reduced. The tube which we used was 260 mm. long and 45 mm. inner diameter.

(2) *The Ice-stirrer.*—The device for using the ice-stirrer is shown in Fig. 1. First there was a carrier for the stirrer frame. This carrier consisted of a brass plate, *a*, with three prongs, which were bent down so as to grip the vacuum tube firmly. Upon the under side of this plate was cemented a cork stopper which fitted the mouth of the vacuum tube nicely. Both the brass plate and the stopper were perforated at the center so as to carry the Beckmann thermometer. At either side of the perforations for the thermometer was placed a smaller perforation, and through each of these perforations was passed a ⅛ inch brass tube, *b b*, which was soldered firmly into the brass plate. In addition to this these two tubes were braced so as to remain in a position parallel to one another, by means of the strips of brass, *c c*. These tubes served as guides for the rods of the stirrer frame proper. The stirrer frame consists of the two upright rods, *d d*, held parallel to one another and in position to follow smoothly through the guides by means of the brass braces, *e e*. At the upper brace, connection is made with a rod which runs to the wheel which moves the stirrer. At the lower end of the rods is soldered the cylindrical roll of silver foil on which the ice is to be frozen, *f*. The stirrer is run very easily by means of a small motor.

(3) *The Freezing of the Stirrer.*—In freezing the ice on to the stirrer frame the following device was made use of (Fig. 2): A piece of glass tube, *a*, slightly smaller than the inner dimensions of the vacuum jacket to be used, was fitted with a rubber stopper carrying another piece of glass tubing, *b*, somewhat larger than the diameter of the thermometer. The stirrer frame of silver foil, *c*, was then placed in the tube, cooled boiled water poured in to the upper level of the frame and the whole apparatus then placed in a freezing-mixture and the water allowed to freeze on the stirrer frame. The stirrer was then easily removed by slightly warming the outer and inner tubes. After removal it was placed in a vacuum jacket for some time before being used in order to avoid having it at a temperature below zero when starting in on

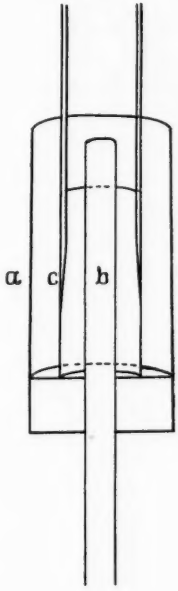

Fig. 2.

the determinations. In this way there was obtained a stirrer of ice that, with reasonable precautions, could be depended on for from six to eight, or even more, determinations without cracking off or becoming too far reduced in size.

(4) In order that the temperature outside the vacuum tube should be held reasonably near to that in the inside of the tube the whole apparatus was packed in a large can of shaved ice.

THE DETERMINATION.

To make a series of determinations the procedure was as follows: About 125 cc. of water, cooled to nearly 0°, was placed in the vacuum jacket and the ice-stirrer placed in position in the tube. After properly adjusting the thermometer, the jacket was placed in the ice-pack and covered over with shaved ice. The water was then briskly agitated with the stirrer, by mechanical means, until the constant reading of the thermometer showed that equilibrium had been obtained. The stirrer and thermometer were

then removed to another vacuum jacket, and a weighed amount of the substance to be used was added. The ice-stirrer and the thermometer were then replaced in position, the jacket was put into the ice-pack and again thoroughly covered with the shaved ice. The solution was now again briskly agitated by means of the ice-stirrer until equilibrium was attained. Then the apparatus was taken out of the ice-pack, the thermometer and ice-stirrer removed, after allowing them to drip a moment, to the other vacuum tube, and the vacuum tube with water and solute weighed.

By subtracting the weight of the solute and the weight of the vacuum tube the weight of the solvent was determined. Another weight of solute was now added, the stirrer placed in position and the apparatus returned to the ice-pack. The solution was again agitated until equilibrium was attained, the weight of the solvent again determined as before, another portion of solute added and the whole process repeated. This was continued until six different readings were obtained, representing as many different concentrations. The rate of stirring was about 300 per minute, preliminary experiments having shown that this rate gave a reading of the thermometer which did not change when the rate was increased. If the solutions used are not too concentrated, eight determinations could easily be made with one stirrer. No difficulty was experienced in the ice not sticking to the stirrer frame. Boiled water is essential to making a good stirrer, because the presence of air spaces in the ice tends to loosen the ice around the frame, which may cause trouble.

THE RESULTS.

In the gradual development of the apparatus into its present form there were obtained a very large number of results which need not be given here, as they serve merely to illustrate the increasing effectiveness of the apparatus. The results which are given in the following tables are those last obtained when the apparatus was in its most nearly perfect form. That there are still a number of sources of error which we have not as yet eliminated will be shown later. Determinations were made with cane-sugar, and with sodium and potassium chlorides.

For cane-sugar we give here but two series of determinations (Table I), bar-sugar being used in all determinations.

TABLE I.

$C_{12}H_{22}O_{11}$. Series I. Mol. wt. = 342.2.

H_2O. Grams.	Sugar. Grams.	Per liter. Grams.	Normal.	Lowering.	Molecular lowering.
128.60	3.00	23.328	0.068	0.126°	1.848
137.10	10.00	72.939	0.213	0.395	1.853
142.20	20.00	140.647	0.411	0.771	1.875
147.15	30.00	203.873	0.595	1.132	1.900
153.40	40.00	260.756	0.762	1.469	1.928
159.80	50.00	312.891	0.914	1.780	1.947
		Series II.			
131.65	3.00	22.787	0.067	0.122	1.845
137.25	10.00	72.932	0.213	0.395	1.853
142.80	20.00	140.055	0.409	0.766	1.871
148.00	30.00	202.702	0.592	1.124	1.897
154.20	40.00	259.403	0.758	1.463	1.930
160.70	50.00	311.138	0.909	1.775	1.952

The two series here given are the last two performed, and were made under as nearly like conditions as possible. It will be noticed that while all the results are lower than those of Loomis,[1] Raoult,[2] Jones,[3] and Nernst and Abegg,[4] those of the smallest concentration vary the least, the difference being greater as the concentration increases. This is probably on account of the increasing percentage of error due to radiation of heat as the lowering increases.

However, while the results obtained by this method are likely to be low, from the fact that the rapid radiation of heat probably prevents one from obtaining a sufficiently low reading of the thermometer, the tendency in the other method is to obtain too low a reading, because the temperature surrounding the tube is lower than that of the solution used. Again, the freezing out of part of the solvent lessens the volume of the solution, tending to high results.

Corrections are, of course, made for these errors, but these corrections are necessarily more or less arbitrary. Probably the correct lowerings would lie somewhere between those of Raoult and ours, and nearer to Raoult's, because of certain errors still not avoided by our apparatus.

[1] *Ber. d. chem. Ges.*, **26**, 797 (1893); also *Ztschr. phys. Chem.*, **32**, 578 (1900).
[2] *Ztschr. phys. Chem.*, **27**, 617 (1898).
[3] *Ibid.*, **12**, 642 (1893).
[4] *Ibid.*, **15**, (1894).

In passing, attention may be called to the general variations in the results of different investigators, especially those of Jones, where, in some cases, he approximates 25 per cent. higher than any other investigator.

Two series of results using potassium chloride as solute are given in Table II.

TABLE II.

KCl. Series I. Mol. wt. = 74.6.

H_2O. Grams.	KCl. Grams.	Grams per liter.	Normal.	Lowering.	Mol. lowering.
130.52	0.20	1.532	0.020	0.073°	3.554
135.31	0.60	4.434	0.059	0.204	3.432
138.40	1.20	8.656	0.116	0.395	3.404
141.80	2.40	16.925	0.227	0.753	3.323
148.18	4.80	32.393	0.435	1.425	3.282
151.87	7.80	51.359	0.689	2.235	3.245
		Series II.			
129.50	0.20	1.544	0.021	0.072°	3.478
132.90	0.60	4.514	0.061	0.207	3.420
135.45	1.20	8.859	0.120	0.401	3.377
138.39	2.40	17.342	0.232	0.774	3.329
141.80	4.80	33.855	0.454	1.491	3.285
145.45	7.80	53.626	0.719	2.331	3.244

In Table III are given two series of results with sodium chloride as solute.

TABLE III.

NaCl. Series I. Mol. wt. = 58.5.

H_2O. Grams.	NaCl. Grams.	Per liter. Grams.	Normal.	Lowering.	Molecular lowering.
130.70	0.20	1.530	0.026	0.090°	3.441
134.10	0.60	4.474	0.076	0.260	3.399
137.30	1.20	8.741	0.149	0.503	3.366
141.30	2.40	16.985	0.290	0.971	3.344
146.20	4.80	32.831	0.561	1.873	3.334
152.50	8.80	57.704	0.986	3.293	3.334
		Series II.			
131.27	0.20	1.528	0.026	0.090°	3.445
138.75	0.60	4.324	0.074	0.252	3.410
143.45	1.20	8.365	0.143	0.478	3.342
148.25	2.40	16.188	0.276	0.923	3.334
154.90	4.80	30.987	0.530	1.759	3.321
161.90	8.80	54.354	0.929	3.096	3.322

If one takes the trouble to compare our results, as given in the three tables above, with those of Jones,[1] Abegg,[2] Richards,[3] and Raoult,[4] which may best be done by plotting the variation of the molecular lowering with the variation in the concentration, it will be found that they are systematically lower than the others, but, at the same time, are more uniform than any of the others except Raoult's, and in some portions of the curve, also those of Richards. These facts allow us to hope that, when all of the sources of error are eliminated or provided for in some way, our method may give results of the greatest accuracy, and it is our present purpose that the work shall be carried on at an early date.

THE SOURCES OF ERROR.

The chief sources of error which have affected the results above are given here. It may seem strange to those who are familiar with this sort of work that some of these errors were not avoided from the start. The reason is that we have put in all of our time up to the present in perfecting the mechanical part of the method, which at first gave very erratic results. While carrying on this part of the work it seemed wholly unnecessary to work with a too great refinement of method in other respects. Greater or less errors are then due to

(1) The fact that the thermometer used was not calibrated.

(2) The thermometer was not kept continually in ice water when not in use. This should be done, as, when a thermometer has stood at room temperature for some time and is then brought to zero, it takes some hours before the final zero reading is obtained.[5] This is due to the slow contraction of the glass.

(3) The still uncertain effect of variations of the barometer on the readings of a Beckmann thermometer. This is probably a factor that must be separately worked out for each thermometer.

(4) Probably a very considerable source of error arose from the fact that no attempt was made to follow the temperature of the solution at all closely with the temperature of the pack outside. We have reason to believe that there was considerable radiation even across the walls of the vacuum tube.

[1] *Zischr. phys. Chem.*, **11**, (1893).
[2] *Ibid.*, **20**, 207 (1896).
[3] *Ibid.*, **44**, (1903).
[4] *Ibid.*, **27**, 617 (1898).
[5] Compare Richards: *Loc. cit.*

We propose in the near future to see that a thorough test of the apparatus is made, taking account of all known sources of error, and we have reason to hope that the results so obtained will compare with the best of the older investigators.

STANFORD UNIVERSITY,
May 17, 1904.

THORIUM; CAROLINIUM, BERZELIUM.[1]

BY CHARLES BASKERVILLE.

Received June 24, 1904.

SYNOPSIS.

THIS paper presents a brief historical account of the discovery of thorium and the questions raised as to its elementary character.

The published evidence is considered in conjunction with experimental data obtained and the conclusions arrived at that thorium is not a primary radioactive body.

The complex nature of thorium is proved by the conduct of salts with certain organic bases, as phenyl hydrazine, for example. Fractions were had, giving atomic weights from 212 to 252, the original being 232.5.

Pure thorium oxide from several sources was converted into the chloride by heating it, mixed with pure sugar carbon, within quartz tubes during the passage of dry chlorine. A volatile chloride, "weisser dampff" of Berzelius, was obtained decreasing in amount according to the duration and temperature of the reaction. The purified, delicately green oxide obtained from this gave a specific gravity of 8.47 and the element, berzelium, an atomic weight of 212 (tetrad).

The temperature of the porcelain tube was raised and thorium tetrachloride distilled away. The residue in the carbon boat on purification gave a grayish pink oxide with a specific gravity of 11.26 and an atomic weight of (tetrad) 255.6 (carolinium). The new thorium, or that in a large measure freed from the berzelium and carolinium, gave an atomic weight of 220.6 and a white oxide with a specific gravity of 9.2. The original thorium gave atomic weights 232.5 to 232.6 and its oxide had a specific gravity of 10.5.

[1] Presented before the New York Section of the American Chemical Society, April 8, 1904.

The original thorium dioxide phosphoresces under the influence of ultraviolet light, as does zirconium dioxide. Berzelium and carolinium oxides do not respond to this stimulus, while the new thorium glows with increasing luminosity, according to the decrease of the novel substances.

All these bodies are radioactive.

Certain chemical differences are noted, as, for example, the conduct of their salts with organic bases, fumaric acid, etc. Carolinium oxide is soluble in concentrated hydrochloric acid, while berzelium and thorium oxides are not.

Spectral data are wanting, in fact, the limited portions of the spectra (arc and spark) mapped show the bodies identical. The materials are not yet sufficiently pure, nor the spectral data sufficiently complete, to warrant final acceptance, although the preponderance of evidence is favorable to the assumption of the existence of two new members of the family of chemical elements.

The marvelous phenomena of radioactivity, accounts of which have filled our chemical and physical literature for the past six years, have stimulated numerous investigators to take part in asking a solution which would be satisfactory and not wholly drive us from our former conceptions of the fundamental laws of the conservation of matter (whatever it may be) and energy (however we may measure it). Naturally such have had to do with thorium, the radioactivity of which was independently noted by G. C. Schmidt[1] and Curie,[2] and studied extensively from both points of view by Rutherford, Soddy and their co-workers,[3] Giesel,[4] Hofmann and Zerban,[5] Owens,[6] Pegram[7] and others, as well as myself.[8]

Other communications upon our researches on thorium have been withheld in the hope of early reaching a solution of the difficult problems involved in an investigation of that element. While the work is far from complete—is any scientific work com-

[1] *Wied. Ann.*, **65**, 141 (1898).

[2] *Compt. Rend.*, **126**, 15; see also Mme. Curie's Thesis, presented to the Faculté des Sciences de Paris, 1902.

[3] Many papers in *Phil. Mag.*; *Proc. Chem. Soc.*, **18**, 2 (1902), and Transactions, **81-82**, 476 (1902), etc.

[4] *Ber. d. chem. Ges.*, **34**, 3776 (1901).

[5] *Ibid.*, **35**, 533 and 1457 (1902), and **36**, 3093.

[6] *Phil. Mag.*, October, 1899.

[7] *Phys. Rev.*, **17**, 424 (1903).

[8] This Journal, **23**, 761 (1901).

plete?—we think sufficient evidence of the complexity of the element has been accumulated to warrant definite statements and excuse us from having had recourse to that "bastard *a priori* method," according to Herbert Spencer, namely, drawing conclusions from insufficient data. Further, on account of the numerous investigations that are coming out upon the elements of high atomic weights it is well to offer our observations that they may be of service to others.[1]

In 1817, Berzelius,[2] while investigating gadolinite from Korarfvet and another mineral from Finbo, believed he found an unknown oxide similar to zirconia and called it "Thorine," after the mythological Scandinavian god of thunder, Thor. This master chemist, marvelously accurate, especially for the time, soon learned[3] that "thorine" was in fact a phosphate of the yttrium earths and the name properly remained but a short time in chemical literature. In 1828 this same chemist[4] found a new mineral, thorite, on the Island Lövö, near Brevig, Norway. In it he discovered a new element with which he revived the name, thorium; Chydenius[5] completed the investigation and Cleve[6] revised the

1 NOTE—When my first preliminary paper on the complexity of thorium was made known publicly, in a note I gave as an excuse for publishing the work a statement of the fact that I had written Professor Bohuslav Brauner that I thought I had brought about a breaking-down of the element. I requested a sample of the very pure body he had prepared and used in his excellent atomic weight determinations, that I might check my work. I received no acknowledgment of the letter and would not know to this day that it had been received but for what followed. Dr. Brauner shortly published some work which clearly pointed to thorium being composite. Having devoted some years of study to the work myself and following entirely different lines, I immediately, within eight days, at the first public opportunity, presented my paper. For fear I might be misunderstood, the facts outlined above were made known. In a letter to the editor of the *Chemical News*, Dr. Brauner took exception to my statement, assuming an intimation on my part that he had taken advantage of information contained in a private letter. The letter in which I gave no details of the method of procedure was quoted from (so it *was* received); furthermore an excuse was given for not having replied to the letter, that I was interfering with his field. Apparently a large number have interfered with that field since my publication. I purposed saying nothing regarding Professor Brauner's letter, but on account of the earnest solicitation of many friends the above statements are made known. It was utterly foreign to my mind to cast any reflections upon Professor Brauner. I appreciate most keenly his beautiful researches carried out in the rare earths in which field that savant ranks as a master. I must object, however, to his having the field reserved. In fact, our work was carried out upon entirely different lines and similar conclusions reached. While it is only human that one should care to have his work appreciated, yet I am not engaged in scientific work for the credit alone.

2 "Afhandl. i. Physik. Kemi. och Mineralogie," Vol. V, p. 76; *Ann. chim. phys.*, **5**, 8; Schweigger's *Jour*, **21**, 25.

3 "K. Vet. Acad. Handl.," Vol. II, pp. 4, 315; J. B. Berz., **5**, 112 (1824).

4 "K. Sv. Ver. Akad. Handl.," 1829, p. 11; *Ann. Phys.*, **16**, 388.

5 "Kemisk undersökuing of Thorjord och Thorsalter, Helsingfors, 1861, *Ann. Phys.*, **119**, 43.

6 *Bull. Soc. Chim.* (2), **21**, 116 (1874).

older data in 1874. Nilson, with Krüss and Hillebrand, in many researches, determined its atomic weight and secured unquestionable evidence as to its quadrivalence.[1] Quite recently Wyrouboff and Verneuil,[2] for reasons we need not enter into here, brought up the question of the quadrivalence of thorium which really depended largely upon the specific heat values obtained by Nilson.[3] Biltz[4] appears to have settled the matter by a rigid examination of the thorium acetylacetonate of Urbain.[5]

In 1851 Bergmann[6] claimed to have found the oxide of a new element, "donarium," in the yellow variety of thorite, orangite, studied independently by himself and Krautz.[7] Damour,[8] the year following (1852), showed that donarium oxide was impure thorium oxide containing lead and uranium. Bergmann[9] shortly after observed that donarium and thorium were the same. Berlin[10] arrived at the same conclusion, as did Delafontaine in 1863.[11]

Again in 1862 was thorium mistaken for a new element, namely, wasium, reported by Bahr[12] in wasite from Rönsholm. The properties were very similar to those of thorium. Its existence not being clearly defined, Nicklès[13] investigated it, maintaining that it was a mixture of yttrium earths containing didymium and terbium. Delafontaine[14] insisted that it was a mixture of cerite earths and Popp[15] asserted that it was nothing else than yttrium containing cerium. The discoverer[16] shortly announced its identity with thorium and proved its hypothetical existence.

There are not a few instances in the history of chemistry where scientific interest in some particular element or compound has been stimulated directly or indirectly through its commercial application and the demand thereby created. This is particularly

[1] *Ber. d. chem. Ges.*, **9**, 1056 (1876) ; **15**, 2519, 2521, and 2537 (1882) ; **16**, 153 (1883) ; **20**, 1665 (1887) ; *Ztschr. phys. Chem.*, **1**, 301 (1887) ; etc.

[2] *Bull. Soc. Chim.* (3), **21**, 118 (1899).

[3] *Ber. d. chem. Ges.*, **16**, 153 (1883).

[4] *Ann. Chem.* (Liebig), **331**, 334 (1904).

[5] *Bull. Soc. Chim.* (3), **15**, 347 (1896).

[6] *Ann. Phys.*, **82**, 561 (1851).

[7] *Ann. Phys.*, **82**, 568 ; *Ann. Chem.* (Liebig), **80**, 267 (1851).

[8] *Ann. Phys.*, **85**, 555 ; *Ann. Chem.* (Liebig), **84**, 237 (1852).

[9] *Ann. Phys.*, **85**, 556 ; *Ann. Chem.* (Liebig), **84**, 239.

[10] *Ann. Phys.*, **85**, 556, and **87**, 608 ; *Ann. Chem.* Liebig), **84**, 238 (1852).

[11] *N. Arch. Phys. Nat.*, **18**, 343 ; *Jahresber.*, 1863, p. 197.

[12] "Oefvers of K. Vet. Akad. Förhandl.," 1862, p. 415 ; *Ann. Phys.*, **119**, 572.

[13] *Compt. Rend.*, **57**, 740.

[14] *N. Arch. Phys. Nat.*, **18**, 369 ; *Jahresber.*, 1863, p. 201.

[15] *Ann. Chem.* (Liebig), **131**, 364.

[16] *Ibid.*, **132**, 227 (1864).

true of thorium. The first German patent issued Auer von Welsbach[1] marks the creation of unusual interest in the main constituent of his mantle. The improvement in the methods for its extraction on a large scale soon opened the gates wide for numerous researches. Although defined with precision through the work of those mentioned, Nordenskjold,[2] Petterson,[3] Troost and Ouvrard,[4] Berlin,[5] Delafontaine.[6] Bakhuis-Roozeboom, Urbain, Jannasch, Brauner, Kosmann, Chavastelon, Muthmann, Locke, Dennis, Matignon, Böttinger, Moissan, and many others,[7] yet the anomalous conduct of certain of its compounds has caused serious questions, by several investigators, as to its elementary nature.

Chroustchoff[8] reported an element associated with thorium in certain zircons and American monazite sands. Although little information is to be had as to this work, apparently the atomic weight, 220, was attributed to the element, which was detected spectroscopically. As Crookes remarks, "the spectrum of thorium is even more complicated than that of iron," hence further data are necessary. Auer von Welsbach[9] insists that thorium is complex.

In 1898, as adverted to, G. C. Schmidt[10] and Madame Curie[11] independently noted the radioactivity of thorium obtained from Bohemian pitchblende. Not long after the announcement of the Becquerel[12] rays, Crookes[13] showed that by fractioning uranium nitrate with ether, compounds could be obtained which did not affect the photographic plate. This indicated the separation of a new substance (Uranium X) and that radioactivity was not an inherent property of the element uranium, as maintained by Mme. Curie.[14]

[1] *Monatsh. Sci.* (Quesneville) (4), **8**, 2 (1894) ; **Patent List**, p. 136, etc.
[2] *Jahresber.*, **13**, 134.
[3] *Compt. Rend.*, **91**, 232.
[4] *Ibid.*, **102**, 1422.
[5] Pogg. *Ann.*, **119**, 56 (1863).
[6] *Ann. Chem.* (Liebig), **131**, 100 (1864).
[7] Vide the excellent "Index to the Literature of Thorium," Joüet, Smithsonian Miscellaneous Collections, No. 1374.
[8] *J. russ. phys. Chem. Ges.*, **29**, 206 ; *Chem. Ztg.*, 1890.
[9] *Chem. News*, **85**, 255 ; *J. für Gas beleucht u. Wasservers*, 1901, p. 661.
[10] *Wied. Ann.*, **65**, 141.
[11] Madame Curie's Thesis, Faculté des Sciences de Paris (1903).
[12] *Compt. Rend.*, **122**, 420, 501, 559, 689, 762, 1086 (1896).
[13] *Proc. Roy. Soc.*, **66**, 406 (1900).
[14] *Compt. Rend.*, **127**, 175.

Soddy and Rutherford[1] demonstrated that only material carrying the β-rays was thus separated and that the so-called inactive (to the photographic plate) uranium still gave off α-rays, which ionize gases and may be detected by the electrical method. Crookes, in the same paper, reported a few preliminary experiments on thorium compounds and suggested "the possibility of separating thorium from its radioactive substance."[2]

In 1899, Debierne[3] separated from pitchblende a strong active substance which appeared to consist of titanium. On more accurate investigation,[4] however, he proved it to be nearer akin to thorium and having secured an oxide 5,000 times as active as uranium, he named the element *actinium*.

Debierne gives some four methods for separating this element, *to wit*: Precipitation of weak acid solution by sodium thiosulphate, treating the hydroxide with hydrofluoric acid and potassium fluoride, precipitation of the neutral nitrate by hydrogen dioxide and precipitating lead or barium sulphate in the liquid, whereby the active body is carried down. While quantitative physical data, as atomic weight, specific gravity, spectrum, etc., are as yet not to be had, the qualitative conduct of the radioactive properties are fairly well defined.

Hofmann and Zerban[5] examined a number of minerals from which thorium is obtained and proved the presence therein of uranium. The thorium oxides from all of these were radioactive. Norwegian gadolinite, orthite and yttrotitanite free from uranium gave a thorium oxide which neither affected the electroscope nor the photographic plate.[6] The radioactivity of actinium consists primarily of rays or "emanations," simultaneously discovered by Rutherford[7] and the Curies[8] in 1899. The gases emitted by radium and thorium are temporarily radioactive, and may be condensed at —150° and —120°, respectively.

The work of Hofmann and Zerban touching the primary activity of thorium being questioned by Barker,[9] is upheld by the

[1] *Proc. Chem. Soc.*, **18**, 121.
[2] *Loc. cit.*
[3] *Compt. Rend.*, **129**, 593.
[4] *Ibid.*, **130**, 906 (1900).
[5] *Ber. d. chem. Ges.*, **35**, 531 (1902).
[6] *Ibid.*, **35**, 533 and 145 (1902).
[7] *Phil. Mag.*, **49**, 2 (1900); [VI], **5**, 95 (1903).
[8] *Rapports an Congres Intern. de Physique*, **3**, 79 (1900).
[9] "Radioactivity of Thorium Minerals," *Am. J. Sci.*, **16**, 164 (1903).

junior author,[1] who determined the presence of from 0.038 to 0.04 per cent. of uranous oxide in monazite from Bahia and South Carolina. While the uranium obtained from this sand was quite radioactive, the thorium oxide discharged the electroscope in two minutes and forty seconds, two minutes and forty-five seconds, and three minutes and five seconds (the instrument without radioactive substance, three minutes and twenty-five seconds), and the β-activity affected the photographic plate in twenty-four hours. The reasons for this somewhat detailed account will shortly become apparent.

Brauner[2] reported that the heptahydrated thorium tetrammonium oxalate, which he has used in his excellent method[3] for determining the atomic weight of that element, hydrolyzed on diluting its water solution. By this means he obtained two constituents, which he designated thorium α and thorium β and ascribed the atomic weights 220 and 260-280, respectively. No subsequent publication on the subject has come from the Prague laboratory so far. At the same time the writer[4] independently reported the results of his observations, extending over some five years, which pointed toward the existence of a new element associated with thorium and gave it the name *Carolinium*. Since that time I have reported, in fragments, a number of observations in abstract along the same line. They and others are digested in this communication.

While it is unnecessary to recapitulate my first work in the leading paper referred to, it was stated that carolinium was found to be more radioactive than the original thorium. The statement was true for the body in the degree of purity had at that time when examined by the photographic, as reported, and later verified by the electrical method.[5] On page 761[6] it was stated "I am not yet ready to assert that the new substance obtained is not the third radioactive body reported by Debierne in pitchblende, actinium, which he states belongs to the iron group." From what follows it is apparent that carolinium and actinium cannot be the same. In fact, the former has little to do with radioactivity, which is the *raison d'etre* for the latter.

[1] Zerban: *Ber. d. chem. Ges.*, **36**, 3911 (1903).
[2] *Proc. Chem. Soc.*, **17**, 67 (1901).
[3] *J. Chem. Soc.* (London), (Trans.), **73**, 951 (1898).
[4] This Journal, **23**, 761.
[5] This was kindly determined by Dr. Geo. B. Pegram, of the Physics Department of Columbia University.
[6] *Loc. cit.*

The elegant researches of Rutherford and Soddy[1] proved that there can be no doubt of the existence of a novel highly radioactive substance with thorium (thorium X) , as it is usually extracted from minerals without consideration of their chemical composition, to which Hofmann and Zerban strenuously direct attention. Such prepared so-called pure salts of thorium contain a radioactive constituent, which may be concentrated chemically by precipitation with ammonia (the filtrate carries thorium X)[2] and washing the oxide with acid or even water. The residues obtained by evaporation of the ammoniacal solution in the first case are a thousand times as active as the original and "are free from thorium, or, at most, contain only the merest traces, and when redissolved in nitric acid do not appear to give any characteristic reaction" (page 376). Again the residue from the water washings became 1,800 times as active, and after conversion into sulphate, Rutherford and Soddy state, "*No other substance than thorium could be detected by chemical analysis,*[3] although, of course, the quantity was too small for a minute examination."

Having this in mind, the writer requested Dr. H. S. Miner, chemist to the Welsbach Lighting Company, to save certain ammoniacal washings obtained in the process for the extraction and purification of thorium oxide from monazite sand for the manufacture of the Welsbach gas mantles. The ignited residue, obtained from evaporating over 100 liters of this liquor, produced a marked effect upon the photographic plate and showed nearly three times the radioactivity of thorium by the electrical method, using the apparatus of Dolezalek. The radioactivity remained constant through a number of months. The body gave *none of the chemical reactions* and *did not show a single line of thorium in the arc spectrum,* made with a large Rowland grating.[4] Dr. Miner is securing an abundance of this material for us and, as soon as practicable, this will be thoroughly investigated in our laboratory.

The writer, working with Lichtenthaeler,[5] has obtained highly radioactive bodies, tested by the photographic method, from thorium, cerium, didymium oxides and the residual phosphates, ex-

[1] *Proc. Chem. Soc.* (London), **18**, 2 (1902).

[2] Rutherford and Soddy : *Phil. Mag.*, 1902, p. 370.

[3] Italics theirs.

[4] By Dr. W. J. Humphreys of the Broadway Rouss Physical Laboratory, University of Virginia.

[5] Thesis for degree of Master of Science, unpublished.

tracted by ourselves from North Carolina monazite sands. Further, we obtained an extremely active body by precipitating the sulphate solution with hydrogen sulphide, which perhaps would, but not necessarily, indicate the presence of polonium,[1] according to the Curies.

When we consider that barium chloride containing radium may be precipitated by sulphuric acid or silver nitrate and the filtrate or precipitate obtained thereby, supposedly containing none of that remarkable body, is still radioactive,[2] we can easily understand how in a mineral or salt a radioactive body, perhaps resembling one of the constituents, clings to various components throughout many chemical manipulations. It having been suggested that uranium might owe its radioactive properties to the presence of small amounts of polonium or radium, Mme. Curie[3] states that such could not be true and adds in another paper[4] "the property of emitting rays.....which act on photographic plates is a *specific property of uranium and thorium.*" "The physical condition of the metal seems to be of an altogether secondary importance." "Uranium and thorium alone are practically active."

It is very foreign from the intention of the writer to be hypercritical of work which stands out so brilliantly and will remain so for a long time to come, but very painstaking investigations have caused him to face about in this matter, not an unusual condition for scientific truth-seekers. The power possessed by the thorium, as usually prepared, of inducing activity, reported by Rutherford and his co-workers,[5] is deeply interesting and supports our thesis. The brilliant French woman states concerning uranium:[6] "I have never found any marked difference between the relative activities of the same compounds." By analogy one may consistently assume the same for thorium. We have obtained similar compounds of thorium fractions which do differ in their radioactivity, in some cases one being three times as great.

Metzger[7] has published an interesting and novel method for separating thorium from cerium, lanthanum and the didymium

[1] *Compt. Rend.*, **127**, 175 (1898).
[2] See the works of the Curies, Geisel, Elster, and Geitel, Markwald, and others.
[3] *Revue générale des Sciences*, January, 1899; M. and Mme. Curie: *Compt. Rend.*, **127**, 175.
[4] M. and Mme Curie and M. Bémont: *Compt. Rend.*, **127**, 1215.
[5] *Loc. cit.*
[6] *Ibid.*
[7] This Journal, **24**, 901.

depending upon its precipitation from a neutral solution by a 40 per cent. alcoholic solution of fumaric acid. The writer and Lemly[1] have verified these observations as far as ordinary analytical methods are concerned. Applying it to the accepted chemically pure thorium, however, we obtained a filtrate less than 0.5 per cent., which, on evaporation and ignition, gave a grayish oxide possessing such marked radioactivity by the electrical method that Dr. Pegram stated it acted as if "salted with radium."[2] This decayed very rapidly from 42 to 12.4 in eight days, to 3.3 in nine days more (uranium being taken as standard at unity). After thirty-two days more it gave 3 and was practically constant. The corresponding values obtained for the thorium precipitate, which constituted virtually the whole, were 0.63, 0.92 and 1. Truly but one interpretation of these results may logically be had, namely, the existence of a radioactive body with thorium, which is different from it. Crookes has sounded a timely warning against depending upon the photographic method for determining the radioactivity, so we have been guided mainly by the electrical method. Yet most interesting observations may be had by the photographic method, which has been used to secure very rough quantitative results, but by no means comparable to the other procedure. It aids one much in learning the β-activity, whereas the α-rays are the most important factor in the ionization of gases upon which depends the electrical method. Persistent differences in radioactivity of the preparations had by different chemical methods, have been noted and the same method of preparation has given persistent differences in radioactivity measured by the same and different methods.

Rutherford[3] and the Curies[4] have shown that the α-radiations, or "emanations," according to the former, as adverted to, are readily driven away from radium halides and thorium oxide and condensed by liquid air. It does not come within the scope of this paper to discuss the nature of these emanations, which will be dealt with by the author and Lockhart[5] in another communication. Suffice it to say that we have repeated this work success-

[1] Unpublished work.

[2] Personal correspondence. In time Dr. Pegram will no doubt publish a full discussion of all the results.

[3] *Loc. cit.*

[4] *Ibid.*

[5] Soon to be published.

fully and we have applied the same test to a large number of authenticated radioactive minerals, and in every case where those minerals have been known to contain helium we have succeeded in condensing the emanations from them. We have obtained the emanations from uranium- and thorium-bearing minerals, and we have failed to secure emanations condensed on a fluorescent zinc sulphide screen from minerals containing thorium.

The extremely interesting work by Rutherford, with his able associate Soddy and their students, on the regeneration of thorium X, at first thought would apparently convince one that thorium is primarily radioactive, but this can be explained by the presence of minute amounts of a foreign highly active substance, which so far has failed to be sufficiently concentrated for a thorough chemical examination, and yet exercises continually the novel property of inducing radioactivity. It is not hazardous to venture the opinion that it will prove to be actinium. In the light of the facts enumerated, however, it appears that thorium is not primarily a radioactive body any more than water containing a radium salt is primarily radioactive, because the radioactivity appears therein after it is distilled. It must be distinctly understood that no criticism is being passed upon the brilliant investigations progressing so successfully in the McGill laboratory on this extraordinary phenomenon of radioactivity, whatever be its source. It must be remembered that radioactivity is far more delicate than the spectroscope; consequently a notable per cent. of a body possessing that property may be present before any spectroscopic evidence may be had, as noted in Demarçay's work on radium. Further, the compounds of this element exhibit unusual radioactive strength before any change whatever is measurable in the atomic weight of the barium with which it is associated.

Although we have not as yet secured a thorium preparation free from any radioactivity, our observations confirm those of Rutherford and his co-laborers. The conclusion thus arrived at is that thorium, as ordinarily extracted from mixed or complex minerals, contains a primary radioactive body, perhaps similar to the truer thorium, but not necessarily so.

From what has been said, that which follows may be considered as if there were no such thing as radioactivity, as the amount of the body possessing that property is entirely negligible from

a spectroscopic standpoint and far too small to produce the marked physical and chemical changes in pure thorium now to be briefly recounted.

Some years ago the writer and Davis began work on the atomic weight of thorium. A full account of the objections to the former methods will be given in due time. Working with materials from various sources, such variable results were obtained that they could not be attributed to faulty methods. In the light of the research of Brauner and the observations made in this laboratory, the problem resolved itself into securing a pure substance, as free from its contaminating constituents as possible.

In the work of Jefferson and Smith[1] on the separation of the rare earths by means of organic bases, it was stated that thorium gives a yellow precipitate with phenyl hydrazine. Allen[2] remarks that with pure thorium and pure phenyl hydrazine the precipitate is white and quantitative. Although Allen does not state that the source of this material was free from uranium, it may be that both of these observations are correct, as noted previously by the author and Lemly.[3] The precipitate, produced by phenyl hydrazine with very pure thorium, is at first white and gelatinous, but soon acquires color, doubtless due to decomposition of the precipitant. We have observed that fractionation of thorium can be brought about by means of phenyl hydrazine. By addition of an insufficient amount of the reagent one obtains first a heavy flocculent precipitate, which soon acquires color. On addition of more of the reagent there is obtained a gelatinous, white precipitate, which also acquires color as the precipitant decomposes. These substances are different, as shown by variations in the radioactivity, determined by both methods and the solubility of the oxides in hydrochloric acid.

So far we have found it impracticable to fraction thorium compounds on a large laboratory scale with phenyl hydrazine. The gelatinous precipitate clogs up the filtering media we have tried. Upward suction through unglazed porcelain, which has served so satisfactorily in much of the work on the rare earths in this laboratory, failed utterly.

[1] "Aromatic Bases as Precipitants for Rare Earth Metals," this Journal, **24**, 540 (1902).

[2] This Journal, **25**, 421.

[3] Unpublished work. Reported in abstract at the Pittsburg meeting of the American Chemical Society, 1902.

Attention must be directed to the fact that all the different constituents are precipitated by this reagent, but at different rates; hence the speed of the reactions was the point of attack. The difficulty was not one of simple filtration, which may be carried out readily enough after the precipitates have formed and settled, but of rapid separation, thus avoiding a second formidable hindrance, namely, decomposition of the phenyl hydrazine with corresponding variations in the reactions. The use of a centrifuge offered promise. It was successful, and perhaps may be used on a commercial scale, although for reasons which follow it is not recommended. With the machine at our disposal we could work with but 20 cc. at a time. The solution must be weak and a small batch amounted to 10 liters. We regarded it essential that sufficient material be prepared for further purification and investigation, an ample supply being at hand through the generosity of the Welsbach Lighting Company. The writer did not feel that he had more time than the average allotment of life to a chemist, thirty years, so attempted a rough-and-ready settling and decantation with one lot of 10 liters, but with poor success. The old fractional precipitation of the rare earths by ammonia, complained of by Crookes, Hood and others, is mere child's play in comparison with the time-robbing and indefinite fractionation by this aromatic base. A separation of thorium into different constituents was brought about, as shown by atomic weight determinations of different portions. Fractions were had (as tetrad) giving 214, 228, 235, 242, 249 and 252, the original giving 232.5 and 232.6.

This procedure was temporarily abandoned to make use of the method earlier pursued in fractionation and later in the efforts of Dr. Davis and myself to determine the atomic weight of thorium, namely, preparation of the pure crystalline tetrachloride by heating pure thorium dioxide mixed with pure sugar carbon in an atmosphere of chlorine. It is unnecessary, in this paper, to give the details of our procedure, which will be described later in full, further than to say we found it unadvisable to use hard combustion glass tubing as variable amounts of contaminating chlorides were formed from the glass. We found we could not settle upon a definite correction for these impurities, as did Richards[1] in his elegant work on uranium.

[1] "Atomic Weight of Uranium," Richards and Merigold, *Chem. News*, **85**, 177, 186, 201, 207, 222, 229, 249 (1902).

Quartz tubes, 2 cm. in diameter, made to order, were placed within large porcelain tubes, which rested in a powerful combustion furnace. A carbon boat containing the mixture of thorium oxide and carbon was inserted in the end of the quartz tube. Pure chlorine, free from oxygen, was carefully dried as it issued from a cylinder by elaborate desiccating apparatus and led in by means of a smaller quartz tube so that the stream of gas played directly into the boat. Arrangements were made by glass cocks to prevent a back flow of any volatile body that might be produced.

As previously noted, by Berzelius and the author, when this method is followed out, there is obtained a volatile chloride. "weisser dampff," absorbable by alcohol, which, according to the former, is *not* thorium, yet comes from pure compounds of that element. This has been verified by applying the method to thorium obtained from a number of sources, including a small amount of a very pure preparation used by Cleve in his atomic weight determinations and presented to Dr. F. W. Clarke, of Washington, who kindly loaned the preparation to us. It, therefore, appears that the volatile chloride is to be had from thorium itself, or that material which separates with thorium in its extraction from various minerals.

Beautiful fern-like crystals of thorium tetrachloride formed on the inner walls of the quartz tubes. There remained in the carbon boat variable amounts of residue, largely converted into chloride, depending upon the temperature of the furnace and duration of the heating, from two to ten hours. These accumulated residues were converted into the oxide and subjected to similar treatment several times. With each repetition there were diminishing amounts of the volatile chloride and sublimed thorium tetrachloride formed. After the third redistillation the oxide from the residue was digested in hydrofluoric acid and concentrated hydrochloric acid to remove accumulated impurities from the carbon and quartz tube. This oxide is *soluble in concentrated hydrochloric acid,* from which it may be crystallized by evaporation. This is not the novel thorium oxide, Th_3O_5, described by Locke,[1] or that unique compound of thorium which has caused the spirited controversy between Stevens[2] and Wyrouboff and Verneuil.[3] The material thus obtained gave an atomic weight of 241.7 (tetrad).

[1] *Ztschr. anorg. Chem.*, **7**, 345 (1894).
[2] *Ibid.*, **27**, 41 (1901); **31**, 368 (1902).
[3] *Ibid.*, **28**, 90 (1901); **32**, 376 (1902).

This chloride was recrystallized from concentrated hydrochloric acid, three times, until the fine, white needle-crystals appeared the same. The material was converted into the oxide, by solution in water, in which it was readily soluble, giving a perfectly clear solution, absolutely devoid of any opalescence,[1] precipitation by ammonia, and igniting the washed white gelatinous hydroxide in platinum. It was digested in turn with dilute hydrochloric, nitric and hydrofluoric acids, washed with pure water and brought to a constant weight.

In our first published work on thorium some store was laid by the specific gravities of the oxides of the several fractions as a means for watching the course of the disintegration. Some doubt was thrown upon this method of control through work of the writer and Mills,[2] as variations in the value of the same preparations were had depending upon the method employed. It was learned, however, that satisfactory comparable figures were obtained when the oxide was prepared in the same way each time.

The specific gravity of this oxide was determined:

Amount taken. Gram.	Specific gravity.
0.7992	11.25
0.8973	11.27

The specific gravity of the original pure thorium oxide:[3]

Amount taken. Grams.	Specific gravity.
2.0730	10.54
3.4573	10.51

The atomic weight was then determined:[4]

Oxide used.	Sulphate obtained.	Equivalent.	Atomic weight.
1.559290	2.434914	63.875	255.5
0.524254	0.819365	63.975	255.9
0.549331	0.854810	63.900	255.6

The familiar method used was essentially that of G. Krüss with certain variations, namely, a specially devised platinum-lined, asbestos jacketed bath was used and the temperature judged by

[1] See Locke's chloride.
[2] Unpublished.
[3] This work was done by the writer and S. Jordan and will later be published in full.
[4] Unpublished by the author and R. O. E. Davis.

a thermometer in which mercury was under a pressure of twenty atmospheres, capable of registering 560° C. It was standardized by the Reichs-Anstalt.

It is scarcely the time or place to discuss the sulphate method, which will be dealt with fully later. It is well known[1] that the method does not possess the most desirable degree of accuracy, but it answers entirely for such work as is here reported. The treatment with new amounts of sulphuric acid was continued until constant weights were had. It is, perhaps, just as well to state that the weights used were gold-plated and corrected by the Bureau of Standards in Washington; the vibration method was used with a highly sensitive Sartorius balance[2] resting upon a brick-cement pillar and that the pans were so loaded each time with counterpoises and standardized platinized weights as to bring the apparatus to a determined point of the highest sensitiveness. Further, it may not be out of place to state at this point that after removal from the porcelain tube the material used did not come in contact with anything other than Jena glass and platinum; that the water, acids and ammonia used were redistilled in platinum and gave no weighable residues after evaporation. The sulphuric acid was not redistilled, but the very fine product, especially secured, gave no residue on evaporation of 50 cc., and if it had, it would have tended to lower the atomic mass value.

It is here quite interesting to note that Hofmann and Zerban[3] state that the equivalent of "actinium" has been found to be 63.32 or 253.28 atomic weight, whereas that for pure thorium is 58.1, or 232.4 (O = 16). Carolinium oxide shows a radioactivity of 0.56 and 0.6 (original thorium oxide = 1) by the electrical method. The two values were obtained from the same material after an interval of six weeks. Our preparation on heating almost to white heat gave off no "emanation" condensable by liquid air upon a zinc sulphide screen.

The volatile chloride was collected, in part, by its absorption in alcohol and condensation as acicular crystals in the cooler portions of the porcelain tubes. These were dissolved in water and the whole evaporated to dryness, the oxide digested by turn in hydrofluoric, concentrated hydrochloric and nitric acids, and then

[1] "Rare Earth Crusade," *Science*, N. S.

[2] Constructed for Dr. F. P. Venable; see his work on zirconium, this Journal.

[3] *Ber. d. chem. Ges.*, **36**, 3093 (1903).

dissolved in hot sulphuric acid (1:1), the gelatinous white hydroxide precipitated by ammonia, washed, and ignited to a constant weight in platinum.[1]

The specific gravity of this oxide was determined:

Amount taken. Grams.	Specific gravity.[2]
1.9207	8.442
1.8465	8.512

The atomic weight obtained, assuming its tetravalence:

Oxide used.	Sulphate found.	Equivalent.	Atomic weight.
0.306778	0.505705	53.375	213.5
0.320618	0.530890	53.000	212.0
0.794692	1.309245	53.175	212.7

It is very interesting to note that the oxide obtained from this volatile chloride possesses very slight radioactivity, about one-third that of the original thorium, when tested by the electrical method. An exposure to a sensitive photographic plate for seventy-two hours showed that it possesses radioactivity which affects the photographic plate to a very limited degree. It does not give off emanations condensed at the temperature of liquid air, as judged by the effect on a phosphorescent zinc sulphide screen.

Although we know that this material is not yet pure, for reasons which will be given in the following, the novel properties mentioned above and its contrasting chemical conduct enumerated below warrant the statement that we have a new element. Berzelius was the first to observe the formation of this "weisser dampff." On account of his beautiful pioneer researches in the difficult field, as the discoverer of thorium from which it comes, it is only proper that it should bear his name, so I have designated the element *berzelium,* with the symbol Bz.

Just a few words concerning the new thorium, or thorium freed, in a measure, from carolinium and berzelium, are called for here, as that element will be treated of more fully in a later communication. In our former paper[3] the values obtained for the atomic weight of thorium from the tetrachloride were 222-223.3. It was

[1] I have been assisted in this part of the work by P. Irwin.

[2] On page 766, in my former paper (*Loc. cit.*), small amounts of oxides were obtained giving specific gravities 8.77, 8.47, and 11.26.

[3] *Loc. cit.*, p. 771.

distinctly stated that the values were preliminary and are not to be taken as final on account of the small amount of material used in each determination. More material has been secured, purified by treatment with acids, as mentioned above, and atomic weight determinations made according to the sulphate method.

Following are the values found:

Oxide used.	Sulphate found.	Equivalent.	Atomic weight.
0.425456	0.694934	55.15	220.6
0.740052	1.210405	55.025	220.1

Doubtless Chroustchoff's russium and Brauner's thorium α were quite pure preparations of thorium.

The source of heat for our furnace was gasoline gas, which does not have a constant pressure, consequently there can be no question, but there is present in this middle portion variable, but small, amounts of carolinium and berzelium, and that some thorium is in the two extremes. We have just received a specially constructed electric oven from Heraeus and a Le Chatelier pyrometer, so that the process may be controlled with precision. This apparatus has been purchased through a grant from the Carnegie Institution, received this year.

Although these constituents are not yet in the most desirable and highest state of purity, it became important to learn their comparative conduct under certain influences, physical and chemical.

It may be recalled that Kunz[1] and the author examined the action of ultraviolet light, Roentgen rays, cathode rays, and the complex radiations and emanations of radium rays upon a large number of gems and minerals in the Morgan-Tiffany and Morgan-Bement collections of the American Museum of Natural History in New York. At that time the writer[2] also observed the action on many of the rare earth oxides of ultraviolet light produced by sparking high voltage currents between iron terminals. The dioxides of zirconium and thorium only became phosphorescent under such stimulation. One is radioactive, the other not. Uranium oxide, which is radioactive, did not respond. The new thorium oxide phosphoresced beautifully white on a five-minute exposure, while berzelium and carolinium oxides gave negative results. Carolinium oxide, containing variable amounts of tho-

[1] *Science*, N. S., **18**, 769 (1903).

[2] *Chem. News*, **88**, 262; *Am. J. Sci.* **16**, 465 (1903).

rium, responded in proportion to the latter constituent present. We believe this is perhaps the first application of the method to the examination of material in the course of chemical investigations, as suggested by Kunz and Baskerville.

We have learned that ordinarily accepted pure crystalline thorium chloride, when thrown upon a filter-paper from concentrated hydrochloric acid, may be washed with water, a clear solution resulting. Berzelium and carolinium chlorides act similarly. When thorium is freed from these, the body will remain upon the filter-paper and may be washed with concentrated hydrochloric acid, but as soon as pure water is added, it hydrolyzes and gives a turbid filtrate, acting in exactly the same way that titanium does. This was not suspected, although, after the observation was made (by Jordan in this laboratory), it is no more than one might expect. As zirconium does not act like titanium, the natural inference is that it contains some hindering element, perhaps the earth, reported by Hofmann and Prandtl in zirconium from euxenite.[1]

The hydroxides of these three substances are white and gelatinous, insoluble in ammonium, sodium or potassium hydroxide, readily soluble in the ordinary acids. Carolinium oxide is grayish with pink tinge, thorium, white with merest tendency toward green, and berzelium has a more marked leaning towards green. These remarks are applicable to the substances in that state of purity so far had. The oxides of thorium and berzelium are not soluble in hot, concentrated hydrochloric acid even when the digestion has lasted three weeks. Carolinium oxide dissolves slowly but completely, within a few days and the chloride forms fine crystals on concentration of the solution, quite different from ordinary thorium chloride. All three are readily precipitated by the ordinary thorium reagents, *viz.*, ammonium oxalate, sodium thiosulphate, hydrogen dioxide, potassium periodate, etc. Their salts behave differently with various organic bases. Phenyl hydrazine, after a time in the cold, gives a precipitate which becomes yellow, berzelium red and thorium orange. Pyridine precipitates thorium at once, carolinium slowly and berzelium with extreme slowness and incompletely. Xylidine precipitates both the former, but not berzelium. *o*-Toluidine gives a pinkish precipitate with thorium, a white flocculent one with carolinium and none with berzelium. Thorium is completely precipitated by fumaric acid,

[1] *Ber. d. chem. Ges.*, **34**, 1064 (1901).

carolinium only partially, a clear filtrate being had in both cases. Berzelium is precipitated nearly completely by fumaric acid; the filtrate is rendered opalescent by ammonia, however.

The solutions of none of these gave absorption bands. Dr. W. J. Humphreys, of the Rouss Physical Laboratory, University of Virginia, kindly examined the arc spectra with a Rowland grating, 21 feet in diameter and 20,000 lines to the inch. His examination, covering the region between 3,900 and 5,500, showed some differences between berzelium and the other two, but his conclusion was that the differences in the spectra, or those portions of the three materials which give arc spectra, might be accounted for by impurities, or, at any rate, were not sufficient to warrant the statement from his spectral data that they are not the same.

Small portions of the impure materials have been sent to Sir William Crookes, by request, to be examined in the ultraviolet region with the apparatus used in his beautiful mapping of the spectrum of radium.

SUMMARY.

(1) The preponderance of evidence indicates that thorium is not a primary radioactive body.

(2) There can be no question from the work of Chroustschoff, Brauner, Crookes, Rutherford, Auer, and the author but thorium is complex and not a chemical element, as we accept the term.

(3) From the experimental data, physical and chemical, outlined in this communication, it appears that thorium has been resolved into at least three simpler substances and that they are sufficiently identified to deserve distinct names.

(4) The conservative position, in which the author coincides, concerning the acceptance of novel members of the family of elements, is the requirement of spark spectral confirmation. At the same time it must be kept in mind that even spectral work requires unification.[1]

(5) As stated above, one of the objects of this paper is to present work to guide others and seek confirmation in other hands. While we shall be busied with the investigation, instead of asking a reservation, we would invite others to assist in solving the problem.

UNIVERSITY OF NORTH CAROLINA,
April, 1904.

[1] See my address before Section C., A. A. A. S., St. Louis meeting, December, 1903.

ADDENDUM.

Since the paper was written and presented, a letter from Sir William Crookes has been received, excerpts from which are given herewith. "I had not quite sufficient to enable me to photograph the whole ultraviolet spectrum, but I have taken that portion, between wave-lengths 3444.020 and 4071.903, which contain some very characteristic thorium lines. I compared the spectra with my standard thorium spectrum taken from the spark between the poles of metallic thorium. Making allowance for the fact that my spectrum is from the metal, while that from your material is from the chloride solutions, all five spectra are practically identical, all the prominent lines being seen in each spectrum, while there are no lines in one which are not seen in the others..... You must not attach too great importance to these spectrum results. All I can say is that they give no positive proof of the existence of anything new. But they by no means prove that such bodies do not exist. They may be there with their spectra, masked by the thorium, which is present."

As only a limited portion of the spectrum was examined, the question is still an open one. My sincere thanks are due Sir William Crookes.

June 18, 1904.

RUTHENIUM, VI: THE BROMIDES.

By Jas. Lewis Howe.

Received June 24, 1904.

In order to determine whether the bromides of ruthenium correspond to the chlorides, several members of the different series have been prepared and are described in this paper. It was found that the salts of the bromruthenite, X'_2RuBr_5, 'aquo'-bromruthenate, $X'_2Ru(H_2O)Br_5$, and bromruthenate, X'_2RuBr_6, series differ very slightly from the corresponding chlorides, but are rather more soluble and more easily decomposed. This has rendered their preparation, and especially their purification, more difficult, so that sufficient time only has been put upon them to learn their general character.

The bromruthenous acid was prepared by the action of hydrobromic acid upon ruthenium tetroxide, RuO_4. On covering the

tetroxide with a solution (50 per cent.) of hydrobromic acid the solution at once becomes dark reddish purple, very distinct from the reddish brown of the chlorruthenous acid. The action of hydrobromic acid upon ruthenium tetroxide is much more violent than that of hydrochloric acid, but was, in every case, incomplete, a black residue being left, which is insoluble in acids, including aqua regia. This residue dissolves quite readily, as do metallic ruthenium and most ruthenium salts, in potassium hypobromite, giving, apparently, a solution of potassium ruthenate.[1]

On adding bromides of the alkalies to the solution of bromruthenous acid the corresponding bromruthenites are formed. These are very soluble in solution of hydrobromic acid, but less so in excess of the alkali bromides. The cesium and rubidium salts can be almost completely precipitated by excess of the bromide, even in solutions not strongly acid.

In one experiment the bromruthenous acid solution was precipitated by excess of potassium chloride. The salt formed proved, by analysis (No. 2), to be a nearly pure bromruthenite, showing that in the solution there is present not $RuBr_3$, but H_2RuBr_5, and $\overset{+}{2}\overset{-}{H},\overset{-}{RuBr_5}$ rather than $\overset{+++}{Ru}$, $3\overset{-}{Br}$. While this would be expected from analogy to the salts of the type $X'_2M^{IV}Cl_6$, it has possibly not been shown for those of the type $X'_2M'''Cl_5$.

The bromruthenites, when treated with water, give an intensely dark blue solution, which becomes reddish brown and eventually reddish purple on warming with hydrobromic acid. This is unlike any of the chlorine compounds of ruthenium of similar type. On boiling with dilute alcohol in acid solution the bromruthenites undergo an analogous change to that shown by the chlorruthenites, the solution becoming less deeply colored (though still deeply colored in comparison with the aquo-chloride solution). This solution, which contains the aquo-bromruthenate, $X'_2Ru(H_2O)Br_5$, darkens on the addition of bromine water, forming the bromruthenate, X'_2RuBr_6. In this respect there is complete analogy between the chlorides and bromides of ruthenium.

[1] A portion of this insoluble residue weighing 0.1105 gram, after drying to constant weight at 100°, lost, on heating in hydrogen, 0.0424 gram, of which 0.0062 gram was bromine. This bromine was doubtless from either HBr or H_2RuBr_5 which had not been completely removed from the insoluble compound. Allowing for this, the per cent. of ruthenium is in the former case 65.26, in the latter 64.73. This corresponds to $RuO_{3.4}$ or $RuO_{3.5}$. $Ru(OH)_3$ requires 66.6 per cent. ruthenium, and it is thus probable that the black residue is an insoluble hydroxide corresponding to either Ru_2O_3 or possibly RuO_2.

The bromruthenates, like the bromruthenites, are turned intensely blue by water, unless much hydrobromic acid is present. This blue solution of the bromruthenate, if quite dilute and no free acid is present, becomes purplish brown on boiling, and gives then a fugitive purple on the addition of a drop of hydrochloric acid. This reaction is also characteristic of the chlorruthenates. When boiled with acid alcohol the bromruthenate is changed back into the aquo-bromruthenate. The bromruthenates crystallize in minute octahedra, giving a black powder with a purplish sheen, while the chlorruthenates are similar except that the sheen is green. The aquo-bromruthenates are the most soluble of the ruthenium bromides and very difficult to crystallize. They resemble closely the aquo-chlorides. From experimental difficulties in preparation the analyses of the aquo-salts leave much to be desired. The bromine salts of ruthenium which have been prepared are the following:

K_2RuBr_5	$K_2Ru(H_2O)Br_5$	K_2RuBr_6
Rb_2RuBr_5,H_2O	$Rb_2Ru(H_2O)Br_5$	Rb_2RuBr_6
Cs_2RuBr_5,H_2O		

EXPERIMENTAL PART.

The analysis of these salts has been carried out as previously described,[1] except that in some cases the bromine was determined by collecting the hydrobromic acid evolved in a measured excess of N/5 $AgNO_3$ and titrating the excess with N/20 KSCN.

Only after the analyses were completed was it noted that in most cases the bromine removed in the hydrogen stream was high, while that left with the alkali metal after heating was correspondingly low. The hydrogen was dried by passing through two small sulphuric acid wash-bottles, but it evidently contained sufficient moisture to slightly decompose the alkali bromides at the temperature used. Unfortunately it was too late to verify this suggestion by testing the solution of the alkali bromide for free alkali.

Potassium Bromruthenite, K_2RuBr_5.—(1) Formed by addition of potassium bromine to solution of RuO_4 in hydrobromic acid and evaporation over concentrated sulphuric acid. Small brown crystals, very soluble in dilute hydrobromic acid and very soluble with decomposition in pure water. 0.3487 gram.

[1] This Journal, **23**, 783 (1901).

(2) Precipitated by addition of concentrated solution of potassium chloride to a concentrated solution of H_2RuBr_5. Similar to (1). 0.4352 gram.

	1.	2.	Theory.
Ruthenium	17.49	17.05	17.54
Bromine (with ruthenium)	39.49	43.97	41.38
Potassium bromide	40.64	39.41	41.08

A double chloride and bromide of ruthenium and potassium, $2KCl.RuBr_5$, would require 20.73 per cent. ruthenium, 48.88 per cent. bromine, and 30.39 per cent. potassium chloride.

Rubidium Bromruthenite, Rb_2RuBr_5,H_2O.—(3) Precipitated by rubidium bromide from a solution of H_2RuBr_5, and recrystallized from dilute hydrobromic acid. 0.2830 gram.

	3.	Theory.
Ruthenium	15.48	14.73
Bromine (with ruthenium)	36.71	34.74
Rubidium bromide	46.18	47.91

Cesium Bromruthenite, Cs_2RbBr_5,H_2O.—(4) Precipitated by cesium bromide from solution of H_2RuBr_5. Fine black needles. 0.3053 gram.

	4.	Theory.
Ruthenium	14.59	12.95
Bromine (with ruthenium)	32.51	30.54
Cesium bromide	49.84	54.24
Water	2.46	2.29

Potassium Aquo-bromruthenate, $K_2Ru(H_2O)Br_5$.—(5) Potassium bromruthenite was boiled with alcohol and hydrobromic acid, and evaporated. Minute brown crystals separated out on standing. 0.5809 gram lost 0.0029 gram in sixteen hours at 90°, 0.0032 gram additional in six hours at 140°, 0.0011 gram on further heating sixteen hours at 140°. In twenty hours heating at from 200° to 240° it had not become completely dehydrated.

	5.	Theory.
Ruthenium	16.44	17.01
Bromine (with ruthenium)	43.41	40.13
Potassium bromide	38.60	39.84
Water	2.24	3.01

Rubidium Aquo-bromruthenate, $Rb_2Ru(H_2O)Br_5$.—(6) Ruthenium bromruthenite was boiled with dilute alcohol and hydrobromic acid, and evaporated over concentrated sulphuric acid. A brownish black crystalline mass, but no good crystals.

0.1506 gram lost 0.5 per cent. of water at 140°; 2.06 per cent. in eight hours at 200°; on further heating it began to lose bromine.

	6.	Theory.
Ruthenium	16.20	14.73
Bromine (with ruthenium)	35.78	34.74
Bromine (with rubidium)	21.32	23.17
Water	2.06	2.61

Potassium Bromruthenate, K_2RuBr_6.—(7) A concentrated solution of aquo-bromruthenate was cooled to 0°, and through this was passed a current of bromine gas. A precipitate of very minute crystals was formed, which was filtered by suction on a Hirsch funnel, and washed with a few drops of hydrobromic acid. As the acid touched the salt it became instantly indigo-blue. The salt when dry is black with purplish sheen, and consists of minute octahedra. It is very soluble. 0.2992 gram.

	7.	Theory.
Ruthenium	15.54	15.42
Bromine (with ruthenium)	48.27	48.48
Bromine (with potassium)	22.79	24.24

Rubidium Bromruthenate, Rb_2RuBr_6.—(8) A concentrated solution of aquo-bromruthenate was treated with several drops of bromine and allowed to stand over night. Gave minute black octahedra, resembling those of the potassium salt, but less soluble. 0.1288 gram.

	8.	Theory.
Ruthenium	13.97	13.52
Bromine (with ruthenium)	41.38	42.51
Bromine (with rubidium)	21.74	22.26

WASHINGTON AND LEE UNIVERSITY,
LEXINGTON, VIRGINIA, June, 1904.

[Contribution from the John Harrison Laboratory of Chemistry, No. 80.]

COMPLEX THIOSULPHATES.

By Owen Louis Shinn.

(Crystallography by Amos P. Brown and Charles Travis.)

Received June 14, 1904.

(A) CUPROUS-SODIUM-AMMONIUM THIOSULPHATE.

When a concentrated solution of sodium thiosulphate is added to an ammoniacal solution of a copper salt and the mixture allowed to stand for a short time, a mass of deep blue crystals separates. These crystals are stable in the air, are soluble in ammonia, but are decomposed by water. Upon analysis they show the presence of sodium, copper, thiosulphuric acid and ammonia. It was found impossible to completely purify the salt, as even the ammoniacal solution decomposes on standing. The material used for analysis was recrystallized once from ammonia. The results of the analysis were rather confusing, a total of over 101 per cent. being obtained, although they were concordant. The search for an explanation of this yielded a rather surprising fact, *viz.*, the copper was present in the cuprous and not in the cupric condition. This, however, was found difficult to demonstrate in a quantitative way. It was thought that ordinary oxidizing agents, like potassium permanganate or hydrogen peroxide, could be used to oxidize the cuprous oxide and the quantity thus determined. This, however, was not the case, the great readiness with which the solution of this salt absorbs oxygen from the air rendering any quantitative work in that line of no value. Duplicate samples, treated as nearly as possible in the same way, gave results differing by several per cent. It was found, however, that if the finely ground salt be quickly dissolved in ammonia, the solution just decolorized with dilute sulphuric acid and ammonium thiocyanate added, that a white precipitate of cuprous thiocyanate is thrown out and the supernatant liquid gave no reaction for copper with potassium ferrocyanide. Any interruption in this process which permitted oxidation produced a filtrate which gave the characteristic red color of cupric ferrocyanide.

Various attempts were made to determine the copper by the thiocyanate method without the use of reducing agents, but again results were obtained which varied greatly, the fact being noted that the longer the operation took the lower the percentage of

copper in the cuprous condition. A synthesis was then tried. Cuprous oxide was made by reducing Fehling's solution by grape-sugar and, after thoroughly washing, was dissolved in ammonia. The solution thus obtained, which was almost colorless, was treated with a boiled solution of sodium thiosulphate and allowed to stand over night in a closed flask; the next morning the liquid was still almost colorless, but a crop of the blue crystals were in the bottom of the flask. This was looked upon as reasonable grounds for assuming all the copper to be in the lower state of oxidation and leads to the presentation of the formula

$$Cu_6Na_8(NH_4)_2S_{16}O_{24}.6NH_3,$$

or

$$3Cu_2S_2O_3.4Na_2S_2O_3.(NH_4)_2S_2O_3.6NH_3.$$

The analytical results are:

	Cu_2O.	Na_2O.	S_2O_2.	NH_3.	H_2O.	Total.
Calculated ..	26.69	15.53	48.12	8.53	1.12	99.98
Found	26.51	15.50	47.66	8.66	....	98.33

Schutte[1] and Peltzer[2] have each made this salt previously; they claim, however, that the copper is present in both conditions of oxidation, but both state that "great difficulty was experienced in determining the exact state of oxidation of the copper." Peltzer writes the formula $Cu_2S_2O_3.CuS_2O_3.2Na_2S_2O_3.2NH_3$ without giving any reasons for the assumption that the cuprous and cupric oxides are to each other as 1 : 1.

Schutte does not claim an exact ratio and writes the formula

$$Na_2S_2O_3\left(\begin{matrix}Cu_2'\\Cu''\end{matrix}\right)S_2O_3.NH_3.$$

He claims that it depends upon the conditions just what the relations between the two oxides of copper will be.

In view of the thiocyanate reaction and the synthesis from cuprous oxide it would seem as though these formulas could not be accepted, but that a true cuprous salt is formed, the solution of which readily oxidizes in the air and that both Schutte and Peltzer worked with partially oxidized material.

This salt crystallizes in small needles, which belong to the tetragonal system. It has a rich blue color and, when dry, is fairly stable in the air. When it is added to water, a turbid solution

[1] *Compt. Rend.*, **42**, 1267.
[2] *Ann. Chem.* (Liebig), **126**, 325 and **128**, 187.

results, due to a partial decomposition. Ammonia will dissolve it to a blue colored solution, which, upon standing, will deposit black copper sulphide. Dilute sulphuric acid or acetic acid will dissolve it to a colorless solution, which will give strong cupric reactions after standing for a short time. As Peltzer has described, the salt has a decidedly sweet taste and explodes when rubbed with potassium chlorate.

(B) CUPROUS-SODIUM-SILVER THIOSULPHATE.

When a solution of sodium thiosulphate is added to an ammoniacal solution of a mixture of silver and copper salts, deep blue crystals form after standing for a short time. The crystals of this salt are larger and darker than those of the salt just described. It is not as stable as the copper salt, while it is soluble in ammonia, a crystallization was impossible. When this solution is allowed to stand for a short time silver sulphide will be precipitated. This salt seems to have a definite composition, as varying mixtures of copper and silver gave the same salt as determined by analysis. The difficulty experienced in determining the state of oxidation of the copper in the other salt was encountered here. The same tests which caused the copper to be regarded as cuprous in the other case gave similar results here. The formula may be written,

$$Cu_2Ag_4Na_{10}S_{16}O_{24}6NH_3,$$

or

$$Cu_2S_2O_3.2Ag_2S_2O_3.5Na_2S_2O_3.6NH_3.$$

Results of analysis:

	Cu_2O.	Ag_2O.	Na_2O.	S_2O_2.	NH_3.	Total.
Calculated .	7.93	26.14	17.31	42.90	5.68	99.96
Found	8.59	25.71	17.28	43.10	5.30	99.98

The rather large variation in the observed results from those calculated is due to the fact that the salts cannot even be washed to purify them and consequently are contaminated by mother-liquor, which is of an indefinite composition, depending upon the mixture taken. These crystals, upon exposure to the light, darken, as most silver salts do. When first made they have a deep blue color and are translucent; upon standing, even in a closed bottle,

they become opaque and lose their blue color. They are finely crystallized in the tetragonal system. This salt also has a sweet taste and will explode when rubbed with potassium chlorate.

It was tried to form corresponding salts with all metals which form ammoniacal solutions, but without success in any case. This again would indicate that only univalent metals can enter into this combination. Peltzer,[1] in describing the other salt, states that iron, zinc and silver may be substituted for the cuprous copper, but he does not describe the bodies formed. No body containing zinc or iron could be made during the course of these experiments. These compounds serve to bring copper into closer relationship with the other members of the first group of the periodic system.

CRYSTALLOGRAPHY.

As noted in the general description above, the cuprous-silver-sodium-sulphate, $Cu_2Ag_4Na_{10}S_{16}O_{24}6NH_3$, is obtained in considerably larger crystals than the cuprous-sodium-ammonium-thiosulphate, $Cu_6Na_8(NH_4)_2S_{16}O_{24}6.NH_3$, and our crystallographic investigation has been confined principally to this first salt. The crystals of the copper-ammonium salt are too small to be measured on the reflecting goniometer. Approximate measurements by visual reflections and by the microscope indicate, however, the substantial isomorphism of these two salts, and their optical characters, so far as they were determined, are identical. The crystals of the copper-silver salt are very perfect in appearance and some of them were found that gave good images on the goniometer, These were carefully measured with the following results:

Cuprous-sodium-silver-thiosulphate. Tetragonal-pyramidal, group 8 of Dana.

Axial ratio, $a : c = 1 : 0.8375$.

Forms observed $a = 100$ $s = 212$.
$m = 110$ $-s = 122$.

Angles.		Measured (mean).	Calculated.
$m : m''' = 110 : 1\bar{1}0$		45° 0′	45° 0′
$a : a' = 100 : 010$		45° 0′	45° 0′
$s : s'' = 212 : 2\bar{1}2$		86° 15′	86° 14′
$s : s''' = 212 : \bar{1}22$		57° 48′	57° 48′
$s : m = 212 : 110$	$= -s''' : m'''$	49° 37′	49° 35′
$s : a = 212 : 100$	$= -s''' : a$	52° 20′	52° 19′
$s : -s = 212 : \bar{1}22$		....	24° 58′
$s : -s''' = 212 : 2\bar{1}2$		....	35° 36′

[1] *Ann. Chem.* (Liebig), **128**, 189.

The crystals, Figs. 1 and 2, are prismatic in habit, the unit

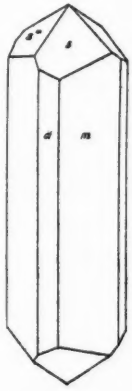

Fig. 1.

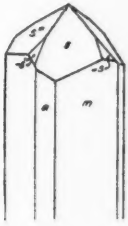

Fig. 2.

prism $m(110)$ and the prism of the second order, $a(100)$, being often equally developed; and they are terminated by the third order pyramid, $s(212)$, Fig. 1, and occasionally show $-s(222)$ along with the pyramid $s(212)$, Fig. 2. The pyramidal planes are usually smooth and give sharp reflections on the goniometer; the prism planes are often striated longitudinally and also diagonally, parallel to the edge $s:m$; and these striations, when present, interfere with good measurement. The measurement on the pyramidal planes, however, was very satisfactory, and the axial ratio determination is practically correct to four places of decimals. No measurements between the plus and the minus third order pyramid faces were made, but the calculated angles are given.

Upon breaking the crystals an imperfect cleavage parallel to the basal pinacoid was observed. No traces of other cleavages were seen.

By transmitted light, deep cobalt-blue. Dichroic: pale saphire-blue for light vibrating $\parallel \dot{c} (= \varepsilon)$; in thin crystals this is nearly colorless; deep cobalt-blue for light vibrating $\perp \dot{c} (= \omega)$. Cross-sections are opaque unless very thin, when they transmit a deep cobalt-blue color by the ordinary ray. Absorption, $\omega > \varepsilon$. Extinction is straight; in very thin cross-section $\perp \dot{c}$ a dusky cross

is seen in convergent light, indicating the uniaxial character. Optically negative as shown by quartz wedge, etc. Satisfactory measurements of the refractive indices were not obtained, but approximate determinations by the microscope method indicated that ϵ was about 1.7.

The cuprous-sodium-ammonium-thiosulphate appears to be isomorphous with the silver salt, but the small size of the crystals prevented exact measurement upon the reflecting goniometer, except by visual reflection. The few angles thus obtained (the prismatic zone) showed the tetragonal character. The habit of the crystals is identical with that of the silver salts, the third order pyramid terminating the combination of the unit and second order prisms. By using the microscope the plane angle between the prism edge and the pyramid-prism edge was measured for both salts and found to correspond within a degree.

The optical characters of the copper-sodium-ammonium salt are identical with those of the silver salt, except that the absorption is stronger in the case of the former. No section that would show the interference figure was obtained with this salt, but it is optically negative, as shown by quartz wedge.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY NO. 100.]

CHANGES IN THE COMPOSITION OF SOME FERROCYANIDES OF CADMIUM, AND ZINC AFTER PRECIPITATION.[1]

BY EDMUND H. MILLER AND M. J. FALK.

Received June 23, 1904.

IN 1897, in discussing[2] two papers read before the New York Section on the "Ferrocyanides of Zinc and of Manganese," the suggestion was made that these complicated precipitates could all be resolved into two ferrocyanides having simple ratios, *i. e.*, $RK_2Fe(CN)_6$ and $R_2Fe(CN)_6$, where R is a dyad metal. This idea was advanced as the alternative to supplying elaborate formulae to the precipitates formed, in order to satisfy the iron-manganese and iron-zinc ratios found by analysis.

[1] Read at the Providence meeting of the American Chemical Society.

[2] Discussion by Miller: This Journal, **19**, 556 (1897).

In 1900[1] it was shown that a particular potassium cadmium ferrocyanide, formed in an ammoniacal solution containing cadmium in excess, which agreed with the formula $K_2Cd_3(Fe(CN)_6)_2$, could be separated into $Cd_2Fe(CN)_6$ and $K_2CdFe(CN)_6$, and that the other potassium cadmium ferrocyanides, when treated with ammonia, yielded invariably $Cd_2Fe(CN)_6$ as the final insoluble product.

It was also shown that these ferrocyanides undergo changes in composition after precipitation, which proceed to definite points under given conditions of acidity and that these changes are hastened by heating.

In 1902[2] an attempt was made to obtain $K_2ZnFe(CN)_6$ and $Zn_2Fe(CN)_6$ from $K_2Zn_3(Fe(CN)_6)_2$, the potassium zinc ferrocyanide obtained in titration[3] by treatment with ammonia. The $Zn_2Fe(CN)_6$ was obtained, but not the other compound. Later the action of ammonia on $Cd_7K_6(Fe(CN)_6)_5$ was studied further by Mr. J. L. Danziger.[4] The ammoniacal solution yielded a white crystalline precipitate containing both ammonium and potassium, besides cadmium and ferrocyanogen in proportions represented approximately by the formula $Cd_8(NH_4)_2K(Fe(CN)_6)_5$; a white precipitate of $Cd_2Fe(CN)_6$ and, finally, crystals of $K_4Fe(CN)_6$. This work was not conclusive, but indicated the formation of an ammonium cadmium ferrocyanide and that the final products were $Cd_2Fe(CN)_6$ and $K_4Fe(CN)_6$.

In 1903 Waring[5] announced a new ammonium cadmium ferrocyanide which gave, on analysis, figures approximating the formula $(NH_4)_2CdFe(CN)_6$. This was obtained in titrating an acid cadmium solution by potassium ferrocyanide in the presence of ammonium chloride.

Waring also stated that the reaction between zinc chloride and potassium ferrocyanide proceeded in two steps: That the normal zinc ferrocyanide, $Zn_2Fe(CN)_6$, was first formed, which subsequently reacted with more potassium ferrocyanide, giving $K_2Zn_3Fe(CN)_6$, and that at 20° C. an end-point was obtained with uranium acetate at the completion of the first stage of the

[1] Miller: This Journal, **24**, 239 (1902).
[2] Miller and Danziger: *Ibid.*, **24**, 827 (1902).
[3] See later.
[4] This work has not been published before.
[5] This Journal, **26**, 13 (1904).

reaction. This work seemed to shed new light on these ferrocyanides and, with the consent of Mr. Waring, the authors of the present paper took up the work again in January, 1904.

CADMIUM AMMONIUM FERROCYANIDES.

In order to confirm the work of Waring the following precipitates were made:

A. Ten grams of cadmium chloride were dissolved in water, 79.8 cc. of hydrochloric acid (sp. gr. 1.20) and 70 grams of ammonium chloride (free from iron) were added and the whole diluted to 2800 cc., then heated to 50° C. and potassium ferrocyanide solution, 44 grams per liter, run in until a very slight excess of ferrocyanide was present. The precipitate was allowed to settle and washed with water till free from chlorides; it was dried over sulphuric acid *in vacuo*, as drying at 100 C. in an air-bath caused a change in color to dark blue-green, due to partial decomposition.

The precipitate was white, slightly crystalline, soluble in hot hydrochloric acid (either concentrated or dilute), and was decomposed by caustic alkali with the liberation of ammonia.

B was made in the same way except that a considerable excess of potassium ferrocyanide was added. Its properties were the same as those of A.

C was made like A, except that the temperature was 100° C. Color, light green.

D was made under the same conditions as B, except that the temperature was 100°C. Color, dark blue.

These precipitates were analyzed by the following method: Half a gram of the precipitate was digested with concentrated nitric and sulphuric acids until decomposed, and evaporated first with nitric and then with sulphuric acids till the solution on dilution showed no blue color. The solution was neutralized with sodium hydroxide, acidified with 4 cc. of concentrated hydrochloric acid and the cadmium precipitated as sulphide. The cadmium sulphide was filtered, dissolved and weighed as cadmium ammonium phosphate, $CdNH_4PO_4H_2O$, and this checked by ignition to pyrophosphate. In the filtrate the iron was oxidized, precipitated by ammonia, dissolved, reduced and titrated by potassium permanganate. The filtrate from the ferric hydroxide was examined for potassium.

Ammonia was determined in a separate portion by distillation with very weak barium hydroxide, 1 to 1.5 grams in 500 cc., so as to prevent any decomposition of the $Fe(CN)_6$ group.

The results were as follows:

	Cd.	NH_4.	$Fe(CN)_6$.
A	1.015	1.95	1
B	1.05	1.92	1
	1.06	1.92	1
C	1.01	1.92	1
D	1.00	1.94	1

A and C, made under the conditions given by Waring, except for temperature, confirm his formula, $Cd(NH_4)_2Fe(CN)_6$. The blue color he reports is due to a partial decomposition, as the precipitates formed at 50° C. and dried *in vacuo* are perfectly white. As the iron-cadmium ratio is 1 : 1.07 in the ordinary titration of cadmium by potassium ferrocyanide,[1] and is 1 : 1 in the presence of ammonium chloride due to the formation of $Cd(NH_4)_2Fe(CN)_6$, it is evident why the addition of ammonium chloride makes a difference in the results obtained in titrating cadmium.

Next, precipitates were made as before, at 50° C. (E) and at 100° C (F), but by pouring the cadmium chloride solution into an excess of potassium ferrocyanide. They were light to dark blue in color and were still further decomposed by drying at 105° C. The ratios obtained, by analysis, were as follows:

	Cd.	NH_4.	K.	$Fe(CN)_6$.
E	0.99	1.4	0.61	1
	0.992	1.4	0.603	1
F	0.995	1.42	0.605	1
	0.996	1.42	0.603	1

These results, which are almost identical, correspond either to $Cd_5(NH_4)_7K_3(Fe(CN)_6)_5$, or to a mixture of $3CdK_2Fe(CN)_6$ and $7Cd(NH_4)_2Fe(CN)_6$.

The formation of such a precipitate is not strange under these conditions. There are present NH_4, K, Cd and $Fe(CN)_6$ ions. Cadmium chloride is added and forms precipitates with either alkali metal and the $Fe(CN)_6$ group, depending on their relative concentration, as the two precipitates are quite insoluble. On the other hand, when the ferrocyanide is added gradually, as in titra-

[1] Miller: This Journal, **24**, 231; also Miller and Fisher: *Ibid.*, **22**, 542.

tion, to a solution containing a high concentration of NH_4 ions the ammonium cadmium ferrocyanide results. The influence of the potassium chloride formed is not to be disregarded, as will be shown later, but if the operation is stopped as soon as an excess of potassium ferrocyanide is present or if the potassium is removed by decantation, as in making the preceding precipitates, its influence is extremely small.

CHANGES IN THE CADMIUM FERROCYANIDES AFTER PRECIPITATION.

It was thought, in 1902, that the action of ammonia on cadmium potassium ferrocyanides might give an ammonium cadmium ferrocyanide with liberation of potassium hydroxide, but this could not be found. Now, assuming the production of $Cd(NH_4)_2Fe(CN)_6$, the action of ammonia may be as follows:

$$2CdK_2Fe(CN)_6 + 4NH_4OH = 2Cd(NH_4)_2Fe(CN)_6 + 4KOH,$$

while the potassium hydroxide, when it reaches a certain concentration, reacts as follows:

$$2Cd(NH_4)_2Fe(CN)_6 + 4KOH = Cd_2Fe(CN)_6 + K_4Fe(CN)_6 + 4NH_4OH.$$

To test this theory some $CdK_2Fe(CN)_6$ was made and analyzed. Two grams were placed in a beaker with 500 cc. of strong ammonia water and stirred mechanically for a week at a temperature of 50° C. The precipitate was then washed with a solution of magnesium sulphate, dried and analyzed. The results corresponded to a formula of $Cd_{16}(NH_4)_6K_2(Fe(CN)_6)_{10}$, or to a mixture of $6Cd_2Fe(CN)_6.3Cd(NH_4)_2Fe(CN)_6$ and $1CdK_2Fe(CN)_6$. (G.)

To test the second half of the reaction alone some dry $Cd(NH_4)_2Fe(CN)_6$ was placed in a beaker with 500 cc. of water and heated; to this was added 1 gram of potassium hydroxide dissolved in water. After being stirred mechanically for one week it was washed, dried and analyzed, and gave values corresponding to $Cd_5(NH_4)_7K_3(Fe(CN)_6)_5$, that is, to the precipitates formed when cadmium chloride was run into potassium ferrocyanide in the presence of ammonium chloride and hydrochloric acid. (E and F.)

These experiments bear out the theory of the action of ammonia, but show that the reaction is incomplete under the conditions used and point certainly to a definite compound which is, at least, a stopping point in the progress of the reaction.

The next experiment was to test the influence of ammonium chloride on $CdK_2Fe(CN)_6$. The precipitate was agitated, as already described, with 50 grams of ammonium chloride and a drop of hydrochloric acid. The results of the analysis corresponded to $Cd_{13}(NH_4)_{12}K_2(Fe(CN)_6)_{10}$, or to a mixture of $3Cd_2Fe(CN)_6$, $6Cd(NH_4)_2Fe(CN)_6$ and $1CdK_2Fe(CN)_6$. (H.) Comparing these results with those obtained by the treatment with ammonia (G), we see that the action is similar, but that it progressed farther with the ammonia, giving a greater proportion of the normal cadmium ferrocyanide, $Cd_2Fe(CN)_6$.

It remained to test the action of potassium chloride on $Cd(NH_4)_2Fe(CN)_6$; this was done in the same way, 70 grams of potassium chloride being used. The precipitate was found to be $Cd_{13}(NH_4)_{12}K_2(Fe(CN)_6)_{10}$, or identical with that obtained by the action of ammonium chloride on the $CdK_2Fe(CN)_6$.

If this reaction were strictly reversible, the resulting compound would be $Cd_{13}K_{12}(NH_4)_2(Fe(CN)_6)_{10}$, but as the substitution of the potassium proceeded only to such a limited extent and the same compound was obtained as before, the conclusion seems to be that there is such a definite compound and that it is the most insoluble of these double ferrocyanides under the conditions.

ZINC FERROCYANIDES.

The precipitate obtained when the zinc titration is made, as is usual in the presence of ammonium chloride, was prepared as follows: Zinc oxide was dissolved in hydrochloric acid, neutralized with ammonia and then hydrochloric acid added so that there were 2 cc. present for every 200 cc. of solution. Seven grams of ammonium chloride were added for every 300 mg. of zinc present, and the solution was titrated at 60° C. till the potassium ferrocyanide was just in excess. The precipitate was washed, dried at 95° C. and analyzed. A slight change in color on drying suggested the presence of ammonia, as the double potassium ferrocyanides were not decomposed on drying at 105° C.

The results of the analysis showed a ratio of

$$Zn : NH_4 : K : Fe = 1.5 : 0.8 : 0.2 : 1,$$

corresponding to the formula $Zn_{15}(NH_4)_8K_2(Fe(CN)_6)_{10}$. So this familiar precipitate is also complex and the change in ap-

pearance noted[1] near the end of the titration in the presence of ammonium or other salts, is probably due to the change from the ferrocyanide first formed to this or some similar compound.

In order to find whether the zinc precipitates, like those of cadmium, would undergo changes after precipitation, some of the precipitate just described was placed in a beaker with 500 cc. of water, 5 cc. of concentrated hydrochloric acid and 70 grams of potassium chloride, heated to 70° C. and stirred constantly for a week. On analysis it was found that the compound had been converted completely into $Zn_3K_2(Fe(CN)_6)_2$, the ferrocyanide obtained when no ammonium chloride is present in the titration.

To test the reverse reaction $Zn_3K_2(Fe(CN)_6)_2$ was treated, as just described, with 50 grams of ammonium chloride. After a week the precipitate was washed, dried and analyzed. It was found to be $Zn_{15}(NH_4)_8K_2(Fe(CN)_6)_{10}$, identical with that obtained in titration in the presence of ammonium chloride.

This work on zinc confirms the results with cadmium and, though the extent of the conversion is not the same with the two metals, it affords further evidence that these precipitates are, in some cases at least, definite compounds, not mixtures.

We believe that Waring's statement that the reaction between zinc and ferrocyanide proceeds in two steps is correct; for, on titrating a zinc solution at 0° C., a yellow color was obtained with uranium nitrate when about half the quantity of ferrocyanide was used. This color faded out in the spot tests on standing, while the usual pinkish brown end-point grows darker on standing. This fact, which has often caused trouble to those not experienced with the method, is explained by the excess of potassium ferrocyanide, which causes the reaction with uranium gradually combining with the $Zn_2Fe(CN)_6$ to form either $K_2Zn_3(Fe(CN)_6)_2$ or the ammonium potassium compound, either of which is less soluble than the uranium ferrocyanides.

The same experiments were tried with cadmium, but the results were not conclusive, as the cadmium ferrocyanide always reacts slightly with the indicator. Tests were also made using other indicators: Cobalt nitrate, green color; ammonium molybdate, yellow; ammonium tungstate, green; ammonium vanadate, red; but nothing was found preferable to uranium nitrate for an acid solution.

[1] Miller and Hall: *School of Mines Quarterly*, **21**, 269.

When the titration of zinc is carried on in an ammoniacal solution, a strong citric acid solution of ferric chloride, when used as a spot-test, gives a very satisfactory end-point and is preferable to copper sulphate. As the normal zinc ferrocyanide is always formed in an ammoniacal solution, whether zinc or ferrocyanide be in excess, this method has the advantage that it is possible to run over with a standard ferrocyanide solution and then titrate back with zinc solution, which is not possible when the titration is done in an acid solution on account of the variation in the composition of the precipitate.

QUANTITATIVE LABORATORY,
June 18, 1904.

ON THE REACTION BETWEEN CARBON DIOXIDE AND SOLUBLE NITRITES.

BY RICHARD B. MOORE.

Received June 15, 1904.

SEVERAL years ago, while working on the preparation of the nitrosulphides and nitroprussides, C. Marie[1] and R. Marquis found that carbon dioxide would liberate nitrous acid from a solution of sodium nitrite. More recently Meunier[2] denied that such a reaction takes place, whereupon Marie[3] and Marquis repeated the following experiments in proof of their contention: (1) Pure carbon dioxide was passed into a solution of sodium nitrite containing potassium iodide and starch paste. A blue color indicated the fact that iodine had been liberated by nitrous acid. (2) A solution of sodium nitrite containing potassium iodide, when shaken with chloroform, gave no coloration, but a similar solution saturated with carbon dioxide turned the chloroform violet. (3) Carbon dioxide was passed through a solution of sodium nitrite and then into a solution of potassium iodide and starch paste, which was turned perceptibly blue.

Meunier claims that the results obtained in the first two experiments were due to the presence of potassium iodide. In order to show this he saturated a solution of sodium nitrite with carbon

[1] *Compt. Rend.*, **122**, 137 and 473.
[2] *Ibid.*, **137**, 1264; **138**, 502.
[3] *Ibid.*, **138**, 367.

dioxide and divided it into two portions. To one of these portions he added a little potassium iodide. After standing some time the solution containing the potassium iodide turned slightly yellow and gave the characteristic tests for iodine with chloroform and with starch. The other portion, which did not contain potassium iodide, at no time gave a test with iodized starch paper, no matter how long it was allowed to stand. With reference to the third experiment of Marie and Marquis, Meunier thinks that the sodium nitrite used contained small quantities of halogen salts, which behaved in a similar manner to the potassium iodide in the first two experiments.

In order, if possible, to obtain conclusive evidence as to whether carbon dioxide does or does not liberate nitrous acid from a solution of potassium or sodium nitrite, the writer performed the following experiments: Three small bottles were taken and partially filled with the following: (*a*) Distilled water, (*b*) and (*c*) strong solution of potassium nitrite. Into (*a*) and (*b*), but not into (*c*), pure carbon dioxide was passed until the liquids were saturated. A strip of iodized starch paper was then suspended in each bottle one-quarter of an inch above the liquid which it contained. Care was taken that the paper should not come in contact with the liquid or sides of the vessel. At the end of three minutes the paper in bottle (*b*) showed a decided change in color, and after six minutes was quite blue. The paper in the two other bottles did not change, even after standing several hours.

The potassium nitrite used was freshly prepared by heating Kahlbaum's special grade of potassium nitrate. The solution was boiled before using.

The above experiment was repeated, only, instead of iodized starch paper, strips of filter-paper, dipped in a solution of metaphenylene-diamine hydrochloride, were used. In bottle (*b*), which contained the solution of potassium nitrite saturated with carbon dioxide, the paper acquired a deep orange-red color in less than two minutes. In the two other bottles the paper showed no change in color at the end of two hours.

On repeating the experiment with solutions of sodium and silver nitrite, instead of potassium nitrite, similar results were obtained.

Filter-paper dipped in a solution of ferrous sulphate was also tried. In bottle (*b*) the paper turned to a yellowish brown in thirty minutes. In bottles (*a*) and (*c*) the paper was entirely

unaffected. That the color was not due to oxidation of the ferrous sulphate is shown by the fact that the change took place in (*b*) in an atmosphere of carbon dioxide, but the paper was unaffected in (*c*), which contained air.

The coloration of a solution of *a*-naphthylamine and sulphanilic acid in acetic acid, noted by Marie[1] and Marquis, was confirmed. Hence the evidence points decidedly towards the conclusion that nitrous acid is liberated from a solution of potassium, sodium or silver nitrite by carbon dioxide.

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THE COLORIMETRIC ESTIMATION OF MAGNESIUM.[2]

BY OSWALD SCHREINER AND WILLIAM S. FERRIS.

Received May 11, 1904.

IN THE course of certain investigations the problem of the determination of small amounts of magnesium in aqueous solutions was presented. It was thought that a possible solution of the difficultly could be found in precipitating the magnesium as magnesium ammonium phosphate, as is done in the ordinary gravimetric procedure, and after washing, to redissolve the precipitate in nitric acid and then to estimate the magnesium indirectly by determining the phosphate with ammonium molybdate, according to the well-known colorimetric method.[3] The idea was tested by evaporating 50 cc. of a magnesium salt solution to a very low bulk or to dryness and using sodium hydrogen phosphate in excess as precipitant, and ammonium hydroxide as wash-liquid. The results were discouragingly high, owing, no doubt, to the difficulty in washing out the sodium hydrogen phosphate from the precipitate and the filter. The more soluble potassium phosphate was, therefore, substituted with far more encouraging results, as will be seen in Table I. In the first two columns in the table are given the actual amounts of magnesium present and found in the tests of 50 cc. of solution used, and in the last two columns the parts of

[1] *Compt. Rend.*, **138**, 694.

[2] Published by permission of the Secretary of Agriculture.

[3] See West-Knights : *Analyst*, **5**, 197 (1880) : Lepierre : *Bull. Soc. Chim.* (3), **15**, 1213 (1896) ; Jolles and Neurath : *Monatsh. Chem.*, **19**, 5 (1898) ; Jolles : *Arch. f. Hygiene*, **34**, 22 (1899) ; Woodman and Cayvan : This Journal, **23**, 96 (1901) ; Woodman : *Ibid.*, **24**, 735 (1902) ; Veitch : *Ibid.*, **25**, 169 (1903) ; Schreiner : *Ibid.*, **25**, 1056 (1903).

magnesium per million parts of solution. The four tests had been treated with varying amounts of phosphate as precipitant, the quantities in Nos. 3 and 4 being many times in excess of the required amount.

TABLE I.—PRELIMINARY TEST.

Gram magnesium.		Parts Mg per million of solution.	
Present.	Found.	Present.	Found.
0.000247	0.000241	4.94	4.82
0.000247	0.000244	4.94	4.88
0.000247	0.000273	4.94	5.46
0.000247	0.000259	4.94	5.18

A more thorough series of tests, both with solutions containing only magnesium, as well as those in which other salts were present, was then undertaken. A great many details of procedure had to be worked out, but it is needless, in this connection, to give every step in the development of the procedure. All the determinations, however, are given in Table II, although many were obtained under unfavorable circumstances for the best results.

TABLE II.—RESULTS OBTAINED WHILE DEVELOPING THE METHOD.

Gram magnesium.		Parts Mg per million of solution.	
Present.	Found.	Present.	Found.
0.000316	0.000296	6.32	5.92
0.000316	0.000289	6.32	5.78
0.000316	0.000252	6.32	5.04
0.000316	0.000255	6.32	5.10
0.000158	0.000148	3.16	2.96
0.000158	0.000152	3.16	3.04
0.000158	0.000143	3.16	2.86
0.000158	0.000141	3.16	2.82
0.000079	0.000102	1.58	2.04
0.000079	0.000078	1.58	1.46
0.000079	0.000101	1.58	2.02
0.000040	0.000070	0.80	1.40
0.000040	0.000057	0.80	1.14
0.000040	0.000056	0.80	1.12

The most serious difficulty expected was the effect of the presence of calcium, which, it was thought, would also precipitate phosphoric acid; but it was found that the calcium was readily prevented from taking part in the reactions by adding a few drops of a solution of ammonium oxalate before adding the phosphate reagent. The facts ascertained while running the above series led to the adoption of the following procedure:

METHOD FOR DETERMINING MAGNESIUM COLORIMETRICALLY.

The following reagents will be required:

(1) *Ammonium Molybdate Solution.*—Fifty grams of the pure salt in 1 liter of solution.

(2) *Nitric Acid.*—Specific gravity 1.07.

(3) *Standard Phosphate Solution.*—0.5045 gram of pure freshly crystallized sodium phosphate, $Na_2HPO_4.12H_2O$, is dissolved in water, 100 cc. of nitric acid (sp. gr. 1.07) added, and the whole diluted to 1 liter. The nitric acid is added to lessen the contamination with silica from the glass. One cc. = 0.0001 gram P_2O_5, = 0.0000342 gram Mg.

(4) *Standard Colorimetric Solution.*—This is prepared by diluting 10 cc. of the standard phosphate solution (3) to about 80 cc. and then adding 9 cc. of nitric acid (2) and 8 cc. of ammonium molybdate solution (1) and making up to 100 cc. After standing twenty minutes it is ready for use. Each cubic centimeter of this colorimetric solution is equal to 0.00001 gram P_2O_5, = 0.00000342 gram Mg.

(5) *Ammonium Hydroxide.*—Reagent.

(6) *Ammonium Hydroxide Wash Liquid.*—One part of strong ammonia water (sp. gr. 0.9) and 9 parts of water. This liquid should be practically free from silica, and for this reason is best prepared from redistilled ammonia water.

(7) *Ammonium Oxalate.*—Saturated solution.

(8) *Phosphate Reagent.*—Dissolve 17.4 grams of potassium hydrogen phosphate, K_2HPO_4, 100 grams of ammonium chloride, NH_4Cl, in about 900 cc. of water, add 50 cc. of strong ammonia water (sp. gr. 0.9) and dilute to 1 liter. One cc. of the solution will precipitate 2.4 milligrams of magnesium.

(9) *Filter-paper.*—This must be free from silica. Schleicher and Schüll's No. 589 or 590 7 cm. has been found to be very satisfactory for this colorimetric work.

Colorimeters.—Two different colorimeters were used in the course of the work. The first instrument was similar to the one described and illustrated by Whitson.[1] It consists of a tube of colorless glass 1 x 10 inches, with a side delivery tube near the bottom to connect by means of a rubber tube with a sliding reservoir for quickly changing the length of the standard colorimetric solution;

[1] Bulletin 85, Wis. Agr. Expt. Station.

a comparison tube, also of colorless glass and as nearly as practicable of the same dimensions as the measuring tube. It is provided with a 50 cc. and 100 cc. mark. The measuring tube is graduated so that one division of the scale is exactly equal to 0.01 of the distance between the bottom of the comparison tube and the 100 cc. mark. Both tubes have accurately ground and polished bottoms. The whole is mounted in a suitably constructed camera. A reflector of white paper, in place of the mirror of the Whitson instrument, at the top of the camera, illuminates the two solutions alike, while the images are viewed in a mirror below.

In the second instrument the length of the standard solution column is varied by means of an immersion tube inside the standard tube. The tube containing the unknown solution is placed below a similar tube, but not touching the liquid. This tube is used so as to give identically the same kind and size of image for comparison with the image from the standard tube. The length of the standard column is then varied by sliding the comparison tube up or down until its color intensity equals that of the unknown solution. The solutions are illuminated by a white reflector from below and the images are viewed in a mirror above, placed at an angle of 45°. A more detailed description of this colorimeter, together with the use of standard colored glasses instead of colorimetric solutions in connection with it, will appear elsewhere.

The procedure for the method is as follows: Measure out a convenient volume of the solution to be estimated, usually 50 cc., into an evaporating dish, add 1 drop of ammonia water (5), and 2 or 3 drops of the ammonium oxalate solution (7); evaporate to dryness on a water-bath. To the cooled dish add 1 cc. of the phosphate reagent (8), and work up the residue well with a glass rod, and then allow to stand about two hours. The precipitated magnesium ammonium phosphate is then washed as follows: Add about 5 cc. of the ammonium hydroxide wash liquid (6) to the dish, washing down the sides, and then pour the liquid through a small filter (9). Repeat this operation five times, then wash down the filter and funnel until the filtrate measures approximately 50 cc. Then rinse the dish once with about 5 cc. of cold water and pour through the filter in such a way as to wash the filter. Reject the washings and put a clean salt-mouth bottle or other receptacle under the funnel. Add 5 cc. of nitric acid (2) to the dish, working this about with the glass rod and pour through the

funnel in such a manner as to wet all the inside of the funnel. Then wash the dish five times with hot water (about 5 cc. each) and continue washing the filter until about 45 cc. of the filtrate have been obtained. To the cooled liquid add 4 cc. of the ammonium molybdate solution (1), and, after twenty minutes, read against the standard colorimetric phosphate solution (4).

When the color developed is too strong for direct comparison with the standard solution, an aliquot part is read. Great care must be taken to insure a sufficient amount of the molybdate reagents when dealing with larger amounts of magnesium, comparatively speaking. The amounts of nitric acid (5 cc.) and ammonium molybdate solution (4 cc.), given above, are safe only up to about 0.0003 gram of magnesium. Should a larger amount have been used for the test, as indicated by the amount of the precipitate or development of color, it will be necessary to add a second portion of these reagents in order to develop the full color, diluting at the same time with water in such a manner as to keep the concentration of the reagents the same, namely, 5 cc. of nitric

TABLE III.—TEST RESULTS.

Gram magnesium.		Parts Mg per million of solution.	
Present.	Found.	Present.	Found.
0.001265	0.001311	25.30	26.22
0.000949	0.000984	18.98	19.68
0.000632	0.000610	12.64	12.20
0.000632	0.000619	12.64	12.38
0.000474	0.000490	9.48	9.80
0.000316	0.000315	6.32	6.30
0.000316	0.000313	6.32	6.26
0.000253	0.000240	5.06	4.80
0.000253	0.000243	5.06	4.86
0.000190	0.000190	3.80	3.80
0.000190	0.000190	3.80	3.80
0.000158	0.000176	3.16	3.52
0.000158	0.000160	3.16	3.20
0.000127	0.000143	2.54	2.86
0.000127	0.000147	2.54	2.94
0.000127	0.000134	2.54	2.68
0.000063	0.000081	1.26	1.62
0.000063	0.000076	1.26	1.52
0.000063	0.000074	1.26	1.48
0.000063	0.000070	1.26	1.40
0.000025	0.000045	0.50	0.90
0.000025	0.000038	0.50	0.76

acid and 4 cc. of ammonium molybdate solution in every 50 cc. of the solution. This procedure was followed in the case of the first five results given in Table III, the first two of which required even more of these reagents. These larger amounts, comparatively speaking, were included so as to show the range of the method. With the smaller amounts, where the coloration to be read is small, it was found very convenient and much more satisfactory to use a standard for comparison of only half the above strength.

In Table III a series of results obtained with solutions of varying concentrations of magnesium and containing at the same time calcium and potassium sulphates, chlorides and nitrates, is given. As before, in the first two columns the actual amounts of magnesium used in making the test are given, and in the last two columns the parts of magnesium per million of solution.

These results, as well as the earlier series, show that in this procedure the magnesium, and magnesium only, is completely precipitated by the phosphate reagent, and that the loss of the resulting magnesium ammonium phosphate in the course of this brief washing with ammonia water must be exceedingly slight even with the smallest amounts of magnesium used. The tendency towards high results with the exceedingly weak solutions is, no doubt, due to the error introduced by the almost unavoidable color of the reagents themselves, an effect which is wholly negligible and in part compensated by the reagents in the standard, when stronger solutions are used. The actual error, however, as is readily seen by an examination of the figures is no greater in these low concentrations than in the higher ones, although it is naturally a much greater per cent. of the amount present.

As silica gives the same coloration with the molybdate reagents, it is, of course, essential that this disturbing factor be removed. As an alkaline fluid is used throughout the procedure, it is evident that the dissolved silica will remain throughout in solution and be removed in the rejected wash liquors. As ammonia water always contains traces of dissolved silica, the last washing, as directed above, is always made with pure water. In order to show experimentally that silica, present in the original solution, is completely removed in the procedure, a series of solutions of varying concentrations in magnesium, but all containing more than five parts of silica per million of solution, were made. Calcium and potassium salts were also present. The results of the magnesium determinations are given in Table IV.

TABLE IV.—TEST SERIES CONTAINING SILICA.

Gram magnesium.		Parts Mg per million of solution.	
Present.	Found.	Present.	Found.
0.000316	0.000313	6.32	6.26
0.000316	0.000316	6.32	6.32
0.000158	0.000147	3.16	2.94
0.000158	0.000151	3.16	3.02
0.000079	0.000094	1.58	1.88
0.000079	0.000088	1.58	1.76
0.000040	0.000055	0.80	1.10
0.000040	0.000054	0.80	1.08

The results clearly show that the silica has been entirely removed in the washing process.

The practical handling of the method as routine work by the assistants in charge of the investigations requiring the accurate determination of small amounts of magnesium has proven very satisfactory and expedient. With proper attention to details one man is able to make twenty determinations, including all calculations, in a working day of seven hours.

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THE ESTIMATION OF SMALL AMOUNTS OF FERRIC IRON BY ACETYLACETONE (ESPECIALLY APPLIED TO WATER ANALYSIS).

BY H. B. PULSIFER.

Received June 28, 1904.

IT IS less than twenty years ago that Combes[1] first prepared acetylacetone and its metallic salts. He mentioned that acetylacetone gives an intense red coloration with ferric salts.

The following was undertaken to ascertain the limits and conditions attending this color reaction, and to compare its value with that of other reagents commonly used to estimate iron qualitatively and quantitatively.

Acetylacetone is a colorless liquid, boiling at 137°. Combes showed its structure to be $CH_3.CO.CH_2.CO.CH_3$. One of the hydrogen atoms attached to the middle carbon atom is easily replaceable by the common metals.

[1] *Compt. Rend.*, **105**, 868.

To prepare the metallic acetylacetonates we have the simple procedure of treating the metallic hydroxide with acetylacetone and crystallizing from alcoholic solution.

Ferric acetylacetonate is, accordingly, made by shaking ferric hydroxide with an alcoholic solution of acetylacetone. On concentrating or cooling the hot saturated solution the salt separates in handsome dark red crystals. The streak of fine powder is a clear orange-red. Solutions containing ferric ions and acetylacetone react immediately to form the colored salt. If there be much of the salt present, the color is deep red by transmitted and orange-red by reflected light. More dilute solutions are orange-red by transmitted and yellow by reflected light.

In its water solution it is probably only very slightly dissociated, as shown by the conductivity measurements made by Hantzsch and Desch.[1] It is, however, largely hydrolyzed into ferric hydroxide and acetylacetone. Its saturated water solution, made by shaking excess of the substance with water for twenty-four hours, contained 1.5 grams per liter in solution. Gravimetric determination by evaporating and weighing as Fe_2O_3 gave 1.48 grams. Colorimetric determination against standard solutions gave 1.5 grams. Urbain and Debierne[2] reported it to be almost insoluble in water. On evaporating its solution on a water-bath only ferric hydroxide remains to form the residue. That the water solution is largely hydrolyzed may be inferred from the fact that, while the addition of either acetylacetone or ferric ions to a saturated solution deepens the color, the addition of an acid causes a very great increase in the color. Rosenheim and Cohn[3] have studied the similar behavior of ferric sulphocyanate. In our case the amount of associated ferric acetylacetonate in the saturated solution was found to be only 25 per cent. The determination was carried out as follows: Fifty cc. of the saturated solution were put directly into a shallow tube so that the color could be read without difficulty on looking down through the highly colored liquid. Into another tube was put an excess of acetylacetone and the volume made slightly less than that of the liquid in the first tube by pouring in distilled water. A standard iron solution, which was slightly acid, was now added to the second tube until the colors

[1] *Ann. Chem.* (Liebig), **323**, 1 (1902).
[2] *Compt. Rend.*, **129**, 302.
[3] *Ztschr. anorg. Chem.*, **27**, 280.

matched. This last solution, containing excess of acetylacetone and free acid, would have all its ferric acetylacetonate in the associated condition. The colors matched when 3 cc. of a standard solution containing 0.001 gram iron per cubic centimeter had been added. This calculated to ferric acetylacetonate gives 0.00038 gram per cubic centimeter in the saturated solution. To determine the total iron present in the saturated solution, 2 cc. were transferred to a Nessler tube, excess of acetylacetone and a drop of dilute hydrochloric acid added and the color compared with standard cold tubes, already made up. This gave the total amount of iron present as 0.000235 gram per cubic centimeter. Its value as acetylacetonate is 0.0015 gram. We then have ferric acetylacetonate, as such, 0.00038 gram per cubic centimeter. Total iron and acetylacetone in solution, 0.0015 gram per cubic centimeter Amount of association, 25 per cent. From the fact that the salt is so largely hydrolyzed in solution comes the chief difficulty in using it for the estimation of iron. It is possible, however, to get uniform results by taking the proper precautions as to the amount of acid present.

The delicacy, range, influence of other substances, influence of heat and permanency was, in each case, determined on solutions made up in common 50 cc. Nessler tubes. For this purpose the required amount of standard iron solution was measured into the tube, the reagent added, the tube filled with distilled water to the mark and the contents mixed by twice pouring into a clean tube. Colors could then be read immediately.

The acetylacetone used was Kahlbaum's, freshly distilled, and diluted with water or weak alcohol until it contained only 0.5 per cent. acetylacetone. Two cc. of this 0.5 per cent. solution added to the Nessler tube will furnish sumcient excess of the acetylacetone for as large amounts of iron as can be estimated by this method. Commercial acetylacetone darkens on standing, but distils colorless on the first distillation.

Standard iron solutions of various strengths were made by dissolving 99.98 per cent. iron wire in a few cubic centimeters of hydrochloric and nitric acids. These were then diluted to the required volume. The final solution should not contain so much acid that when it is made up in the Nessler tube for reading it looks pink by reflected light. Standard solutions may also be made

by weighing out ferrous ammonium sulphate and oxidizing before dilution, but, as before, the solution must be only faintly acid at the final dilution.

The least amount of iron that can be detected with acetylacetone is less than that which can be detected by potassium sulphocyanate, as it is commonly used. The following will illustrate the comparison:

STANDARD IRON SOLUTION, 1 CC. = 0.000001 GRAM Fe.

By pipette. cc.	Gram Fe.	2 cc. acetylacetone (0.5 per cent.)	5 cc. KSCN (0.5 per cent.)
1	0.000001	No color.	No color.
2	0.000002	"	"
3	0.000003	Distinct color.	"
4	0.000004	Darker.	"
5	0.000005	"	"
6	0.000006	"	Faintest pink.

Under these conditions the smallest amount of iron that can be detected with acetylacetone is thus 0.000003 gram. The least that can be detected with sulphocyanate is 0.000006 gram. This does not mean that acetylacetone is the most delicate test for iron, but that, under these conditions, it is more delicate than the sulphocyanate. If 5 grams of potassium sulphocyanate are added to one of the tubes containing 0.5 cc. of the above standard solution it will give a distinct pink color. This is 0.0000005 gram of iron in 50 grams of substance. Again, one drop of the same solution, which will contain about 0.04 cc., will be colored distinctly pink if a crystal of solid potassium sulphocyanate is applied. This is a detection of 0.00000004 gram of iron. Experiments made to have acetylacetone detect less than 0.000003 gram of iron were not successful.

The reaction with salicylic acid in the Nessler tube has a sensitiveness quite similar to that of the sulphocyanate, but the color fades rapidly. The reaction with potassium ferrocyanide is not nearly so delicate and the reagent has the disadvantage that it has a strong color of its own.

The range over which acetylacetone is available is somewhat greater than that of the sulphocyanate. The smallest amount that can be detected has already been stated to be 0.000003 gram. The largest amount that can well be estimated in the 50 cc. tube is about 0.0006 gram. Excepting for the smaller amounts, the total amount present can be estimated to at least one-tenth of the

amount present; from 0.00005 gram to 0.0006 gram the accuracy is even better. For instance, if the solution contains about 0.00005 gram, it is not difficult to detect a variation of 0.0000025 gram, and for amounts of about 0.0004 gram it is not difficult to detect variations of 0.00001 gram. Under the same conditions the color produced by sulphocyanate becomes difficult to read, if the tube contains 0.0003 gram iron.

Very few common inorganic salts that can exist in solution with ferric iron have any influence on the color when present in small amounts.

Substances to the amount of 0.2 gram, which will furnish the following ions, have no effect whatever: Na, K, Ca, Sr, Ba, Cl, Br, SO_4, NO_3, ClO_3, Mg, Zn, Pb, Mn, As, Cd, Al and Hg.

Smaller amounts of silicic acid, phosphoric acid and copper do not interfere. Carbon dioxide in solution has no influence. The acetylacetone may be used in water or alcoholic solution, the presence of alcohol not altering the color. Oxides of nitrogen give a brown color with acetylacetone and should be removed from the concentrated solution by boiling. Caustic soda or potash destroys the color and precipitates iron from its solution of ferric acetylacetonate. The iron is not precipitated by ammonia; ammonia gives a strong yellow color to the solution, although the iron can still be estimated by its characteristic color.

Ferric acetylacetonate acts as an indicator, its neutral orange-red solution turning pink with acids and yellow with ammonia. It is not a delicate indicator, hence it can be used for the estimation of iron either in faintly acid solutions, when its color is brown or red; or it can be used in stronger acid solution when its color is a clear pink; or it can be used in solutions distinctly alkaline with ammonia when it has a yellow hue. Solutions once distinctly pink change only slightly on addition of small amounts of acid, but for the best work in pink solutions the amount of acid in all the solutions compared should be uniform. Solutions once distinctly alkaline to litmus with ammonia do not have their color changed by the addition of more ammonia. Considerable variation in the amount of acid may be allowed in the original solution, provided that it is sufficiently diluted before the acetylacetone solution is used. The final 50 cc. Nessler tube should not contain enough acid to have the tube look pink when viewed from the side. The original solution may well contain less than 10 cc. of any dilute

acid. This should then be diluted to 500 or 1000 cc. and portions as small as needed then transferred to the Nessler tube, for under the conditions of faintly acid solution scarcely more than a drop of any one of the common dilute acids is permissible in the Nessler tube. The addition of even one drop of a strong acid to a faintly acid tube weakens and changes the color, two drops has a greater influence and ten drops may remove nearly all the color.

If the original substance contains more than a trace of iron, the final dilution for the best readings of iron will have diluted the other material present so much that it will no longer be present in sufficient quantity to interfere with the accuracy of the determination. If the solution does contain sufficient acid to be pink, it will, of course, be necessary to influence the standards likewise.

There is one serious objection to the use of potassium sulphocyanate for the quantitative estimation of iron; the color first produced immediately begins to fade and continues to fade. An hour's exposure to sunlight will render a solution originally a deep red almost colorless. The color decreases during an hour even in the dark, and considerably more rapidly in diffused light. This is a source of serious error unless great care is used and even then it is a source of constant annoyance. The cause of the fading has been given by Shilton[1] to be due to the reducing action of the sulphocyanate. The color produced by salicylic acid also fades so rapidly that the faintly colored solutions soon lose all color.

The permanency of the color produced by acetylacetone and ferric ions in the faintly acid solutions adds greatly to the usefulness of this reagent. Tubes so faintly acid as to have the brownish or orange-red hues by transmitted and yellowish hues by reflected light showed remarkable permanency. Tubes freshly made up compared exactly with ones made up an hour or even three weeks previously. Strong sunlight altered the hue somewhat. Tubes strongly pink with acid showed some fading on standing a day.

Changes of temperature over small ranges have no appreciable effect on the color of ferric acetylacetonate. Boiling will remove the greater part of the color from a solution red with sulphocyanate. Boiling changes the hue of the solution red with acetylacetone, but the change is only temporary and the original color is resumed on cooling.

[1] *Chem. News*, 234 (1884).

This test for iron can be used in all those places where potassium sulphocyanate has been used. In nearly all cases where it is to be used sufficient dilution for the best readings of the iron will also so dilute the other salts present that they will not interfere with the estimation of the iron. In all cases the residue containing the iron may be taken up in a very few drops of nitric or hydrochloric acid, or both, and largely diluted. An aliquot part of this solution is then transferred to the Nessler tube and the estimation made.

For water analysis, either 100 cc. of the water may be evaporated to dryness on the water-bath and all organic matter removed by sulphuric and nitric acids, or the residue from the total solids may be used. The ferric oxide left from the ignitions is insoluble in nitric acid and is dissolved with difficulty by hydrochloric acid. However, it yields to warming with a few drops of dilute sulphuric acid and a drop of hydrochloric acid.

If much insoluble residue is now present, the solution may be filtered through a very small filter into a porcelain dish. After washing the filter, the iron may all be oxidized by a few drops of hydrogen peroxide or dilute nitric acid. If only traces of iron are present, the solution may be evaporated almost to dryness to expel the excess of acid, transferred to a Nessler tube, 2 cc. of 0.5 per cent. acetylacetone added and the solution made up to the mark with distilled water. If larger amounts of iron are present, the small amount of acid may not need to be removed by evaporation, but the solution diluted to 500 cc. or 1000 cc., and a definite portion of this transferred to the Nessler tube, 2 cc. of acetylacetone solution added and the tube filled to the mark with distilled water. The contents of the tube should finally be thoroughly mixed by twice pouring into a clean tube or beaker.

For occasional analyses standards may be made by preparing the sample, then making the standard to match by putting the 2 cc. of acetylacetone into a tube, partly filling with water, and then adding sufficient standard iron solution to match the sample tube after filling to the mark with water and thoroughly mixing.

For continuous use, standards may be prepared from varying strengths of standard iron solution and kept free from dust and away from direct sunlight.

In no case should colors be matched by pouring out one solution and estimating the iron by the color of the fractionally

matched tubes. Experiments proved that it does not follow that pouring out half of the solution from a tube will leave a color at all comparable with the regular tube containing half the amount of iron. For accurate work the conditions as to acid, excess of acetylacetone and volume should be the same.

Summary.—Of all the reagents that have been used for the quantitative estimation of ferric iron, potassium sulphocyanate has been the most satisfactory. A real source of weakness has been the loss of color attendant on standing for even brief intervals.

Acetylacetone is a reagent equally sensitive under usual conditions; it has greater range; there are almost no substances which interfere when they are present in small amounts, while the color produced in faintly acid solutions has a very considerable permanency.

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DETERMINATION OF PHOSPHATES IN NATURAL WATERS.

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THE potability of water is impaired by the presence of decaying organic matter. In this process of decay one of the numerous changes produced is the conversion of organic phosphorus compounds into phosphates. But the presence of phosphates does not necessarily indicate a source of contamination, because they may also be present as a result of waters charged with carbonic acid percolating through the rocks and minerals. Particularly in the case of streams and shallow wells the water may contain a large amount of phosphates derived from the fertilizers being used on

the adjacent farms. Even the early investigators held that potable waters might contain a large amount of phosphates. In the case of unpolluted waters containing notable quantities of chlorides and nitrates, they are only condemned in the presence of other contaminating ingredients, so, as an additional source of evidence in aiding us in the interpretation of the analysis of drinking-waters, Woodman and Cayvan[1] have called attention to the desirability of phosphate determinations.

Many methods have been suggested for the determination of phosphates in the presence of silica, but until very recently no satisfactory procedure has been devised. Schreiner[2] presented a colorimetric method by means of which both the silica and phosphates can be very accurately determined when present in small amounts. This method is based on the fact that the silicomolybdate gives different depths of color by varying the conditions of treatment, while the intensity of color, due to phosphomolybdates, is the same under these conditions. If the ammonium molybdate and nitric acid are added one hour apart, the color of the silicomolybdate is half as great as the color produced by adding them simultaneously; that is, 50 cc. of a solution of silica are placed in a flat-bottomed tube and 5 cc. of nitric acid (sp. gr. 1.07) and 4 cc. ammonium molybdate are added and this compared with a standard phosphate solution prepared by adding the same quantities of the reagents and reading after twenty minutes; this is designated the "*a*" reading. If another 50 cc. of the silica solution are taken and 4 cc. of ammonium molybdate are added, and at the end of one hour 5 cc. of nitric acid (sp. gr. 1.07) added and in twenty minutes compared with the standard, we have what is designated the "*b*" reading. In the case where there is no phosphate present the ratio of the "*a*" reading to the "*b*" reading is 2:1. If phosphates are present, the difference between the "*a*" and "*b*" readings represent just one-half of the silica coloration and twice this difference subtracted from the "*a*" reading gives the value of the color due to the phosphates.

That 5 cc. is the amount of nitric acid (sp. gr. 1.07) that gives the greatest intensity of color was also ascertained by us before Schreiner's paper came to our notice. In order to test the accuracy of his method and the factor for the determination of silica a

[1] This Journal, **25**, 1056 (1903).
[2] *Ibid.*, **23**, 96 (1901); **24**, 735 (1902).

silicate solution was prepared by dissolving sodium silicate in water, acidifying with nitric acid and standardizing by determining the silica by volatilizing with hydrofluoric acid. The solution was then diluted until 1 cc. contained 0.1 mg. of SiO_2. Then known amounts of this solution were taken and diluted to 75 cc., and, after adding the reagents, compared with a standard which contained 0.01 mg. of P_2O_5 per 1 cc. From the following table it is evident that for all practical purposes the relation of the "*a*" to the "*b*" readings is 2:1 and that the reading for SiO_2 with a P_2O_5 standard is equal to twice the actual value in SiO_2. The heading of the columns are self-explanatory.

TABLE I.

SiO_2 added. Mg.	Readings. "*a*"	Readings. "*b*."	Ratio of readings. "*a*"/"*b*."
0.2	41	20	2.05
0.4	82	40	2.05
0.6	122	61	2.00
0.8	162	82	1.98
1.0	198	98	2.02

This method has recently been shown[1] to be applicable to the determination of phosphates in soil and plant extracts. In natural waters, however, as Schreiner himself has pointed out,[2] the phosphates are frequently very low in comparison with the silica and in the application of this method to the determination of phosphates in drinking-waters, relatively a very considerable error may result. In order to ascertain the maximum and minimum amounts of silica in the several types of water in the State of Illinois some 5,000 or 6,000 analyses by the Illinois State Water Survey[3] were carefully examined.

In Table II, the maximum and minimum amounts of SiO_2 expressed in parts per million, are given for the various types of water designated at the head of the columns.

TABLE II.

	River.	Spring.	Deep well.	Shallow well.
Maximum	11.3	65.3	64.2	51.8
Minimum	5.0	2.3	1.8	4.0

[1] This Journal, **26**, 808 (1904).

[2] *Ibid.*, **25**, 1061 (1903).

[3] Chemical Survey of the Waters of Illinois. Report for years 1897–1902, by A. W. Palmer.

From the data available it appears that the P_2O_5 content ranges between 0.5 and 5.0 parts per million and it is very evident that the silica is in large excess of the phosphates.

It occurred to us that since Schreiner's method gives such good results when the P_2O_5 and SiO_2 are approximately equal or the P_2O_5 in excess, *that if we were to add a quantity of P_2O_5 sufficient to bring the P_2O_5 content of the water up approximately to that of the SiO_2, or in excess of it, that the original amount of P_2O_5, and incidentally the SiO_2, could be readily and very accurately determined.*

In order to test this a series of solutions was prepared containing known quantities of P_2O_5,[1] varying from 0.01 to 0.5 mg. of P_2O_5 and 0.2 mg. of SiO_2 in 75 cc. of the solution. A second series containing the same quantities of P_2O_5, but with 0.4 mg. of SiO_2 was also prepared. These solutions were then treated with a definite quantity of P_2O_5, the reagents added, and the "*a*" and "*b*" readings taken by means of a standard P_2O_5 solution. It was found that a quantity of P_2O_5, equal to 0.4 mg. or more, would give good results when added to the above concentrations of P_2O_5 and SiO_2, but less than 0.4 mg. proved to be much less satisfactory. So it was concluded to add 0.5 mg. of P_2O_5 to the various concentrations and determine the amounts of P_2O_5 and SiO_2 actually introduced into the solutions by carrying out the method as described by Schreiner.

In Table III are given the experimental data for various concentrations of P_2O_5 and SiO_2, to which 0.5 mg. P_2O_5 were added and the solution diluted to 75 cc. In the first two columns are given the P_2O_5 and SiO_2 content of the solutions in milligrams, while in the next two are the "*a*" and "*b*" readings. In the next three columns are the values of the readings which represent the amount of P_2O_5 added to solutions (0.5 mg.), the original amount of P_2O_5 and of SiO_2 present, while in the last two columns are the original amounts of P_2O_5 and SiO_2, calculated from the "*a*" and "*b*" readings and expressed in milligrams per 75 cc. of solution.

From a comparison of the original content of the solutions, as given in the first two columns of the table and the found values

[1] A standard solution of Na_2HPO_4 was prepared by dissolving 2 grams of the substance in 1 liter of water and standardizing by the magnesium ammonium phosphate and also by the ammonium phosphomolybdate methods. The solution was then diluted so that 1 cc. contained 0.1 mg. of P_2O_5. This solution was used for preparing our phosphate solutions and also for the preparation of the standards.

TABLE III.—ADDITION OF KNOWN AMOUNT (0.5 MG.) OF P_2O_5 TO SOLUTIONS OF SiO_2 AND P_2O_5.

Constituents present.		Readings.		Readings for			Found.	
P_2O_5. Mg.	SiO_2. Mg	"a."	"b."	0.5 mg. P_2O_5 added.	P_2O_5. original.	SiO_2. original.	P_2O_5. Mg.	SiO_2. Mg.
0.01	0.20	90	71	50	2	38	0.02	0.19
0.05	0.20	95	75	50	5	40	0.05	0.20
0.10	0.20	100	80	50	10	40	0.10	0.20
0.20	0.20	110	91	50	22	38	0.22	0.19
0.50	0.20	138	120	50	52	36	0.52	0.18
0.01	0.40	130	91	50	2	78	0.02	0.39
0.05	0.40	134	95	50	6	78	0.06	0.39
0.10	0.40	140	100	50	10	80	0.10	0.40
0.20	0.40	150	112	50	24	76	0.24	0.38
0.50	0.40	178	138	50	48	80	0.48	0.40

given in the last two, it will be noticed that there is a very fair degree of accuracy except where the content of P_2O_5 is 0.01 mg. (*i. e.*, 0.13 part per million), but in all others the results are really very satisfactory for such small amounts of P_2O_5 (0.67 to 6.7 parts per million). It is apparent that quantities of P_2O_5 as low as 0.05 mg. in 75 cc., *i. e.*, 0.67 part per million, can be very accurately determined by this means.

This method of adding 0.5 mg. of P_2O_5 to each 75 cc. sample of water was employed in the determination of the P_2O_5 in samples of drinking-water sent to the Water Survey for analysis. A number of the results of the sanitary analysis and the P_2O_5 and SiO_2 determinations are given in Table IV, and the values are expressed in parts per million.

In this paper we have called attention to the confirmation of Schreiner's colorimetric method for the determination of phosphates and silica when the proportion of the latter is not excessively great.

We have extended this method to the determination of phosphates in natural waters, where the proportion of silica to phosphate is frequently large, by the addition of a known quantity of P_2O_5 (0.5 mg. per 75 cc. of sample of water) in order to bring the phosphate content up approximately equal to, or in excess of, the silica.

We have determined the P_2O_5 and SiO_2 in a number of samples of polluted and unpolluted waters.

TABLE IV.

	Number.	Source.	Residue.	Chlorine.	Free NH_3.	Albuminoid NH_3.	Nitrites.	Nitrates.	P_2O_5, parts per million.	SiO_2, parts per million.
Unpolluted waters.	12,020	93-ft. well	664.8	2.15	0.026	0.052	0.013	0.547	2.34	14.4
	12,014	150-ft. well	386.8	3.40	2.960	0.280	0.000	0.040	2.86	16.0
	12,021	Lake Michigan	330.8	3.10	0.016	0.152	0.002	0.160	2.08	7.1
	12,023	Sulphur Spring	334.8	2.50	0.166	0.099	0.000	0.120	0.78	19.7
	12,025	Iron Spring	320.4	2.30	0.320	0.082	0.005	0.115	1.72	18.9
	12,050	Ice	30.8	2.30	0.840	0.130	0.060	0.074	0.91	0.9
Polluted waters.	12,052	25-ft. well (dug)	397.2	13.5	0.05	0.316	0.080	0.92	7.54	10.4
	12,034	30-ft. well (dug)	4146.6	13.3	0.05	0.056	0.004	6.80	1.04	13.6
	12,033	40-ft. well (dug)	615.2	45.0	0.03	0.134	0.013	25.00	8.58	11.4
	12,047	45-ft. well (dug)	1050.4	68.5	0.016	0.120	0.010	5.00	7.80	3.2
	12,035	50-ft. well (dug)	1004.0	82.0	0.054	0.098	0.009	40.00	7.02	13.8
	12,049	100-ft. well	564.0	64.5	0.004	0.044	0.001	10.40	3.38	14.4
	12,040	Crystal Lake	294.0	3.0	0.072	0.124	0.028	3.73	1.82	4.1
	12,041	Branch Creek, above septic tank	323.6	5.2	0.112	0.168	0.060	3.54	0.52	0.7
	12,042	Septic tank.	647.2	42.0	2.000	0.528	0.500	5.50	8.06	8.4
	12,043	Branch Creek, below septic tank	328.4	7.0	0.188	0.164	0.065	3.94	0.13	0.7

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THE TECHNICAL ANALYSIS OF SPIRITS OF TURPENTINE, WITH A NEW METHOD FOR THE DETECTION OF PETROLEUM ADULTERATIONS AND OF WOOD SPIRITS OF TURPENTINE.

By Jno. M. McCandless.

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An act, passed by the last General Assembly of Georgia, provided for the appointment of an inspector of naval stores for this State, forbade the adulteration of pure spirits of turpentine, with petroleum, wood turpentine or other adulterants, and in case of dispute between the party charged with adulteration and the inspector, provides that a properly drawn and sealed sample be sent to the State chemist to decide the issue. In this way it has become my duty to study the existing methods for the analysis of turpentine and the detection of its adulteration. A good review of the previous literature on the subject is given by Worstall in his interesting article in the *Journal of the Society of Chemical Industry*, **23**, 302 (1904), and, as stated by him, this literature is scanty, and the various tests given, including specific gravity, etc., somewhat unsatisfactory. The usual adulterants are petroleum oil, gasoline, rosin spirits, and recently there has been introduced another possible adulterant in the turpentine distilled from pine wood and old lightwood knots, and stumps, sometimes called stump turpentine or stump spirits. Realizing the necessity of personal experience with samples of undoubted purity and previous history, and being well situated for the purpose of obtaining such samples, I secured from different sections of the State a number of samples of genuine turpentine, representing the entire turpentine-producing area of the State. Also a number of samples of wood spirits of turpentine.

As a preliminary test, Dunwoody's 99 per cent. acetic acid test was tried, but without success in detecting known adulterations. The following figures for iodine absorption, specific gravity and flash test were next obtained. The iodine absorption determinations were carried out precisely in the manner prescribed by Worstall,[1] weighing carefully about 0.1 gram of each sample into glass stoppered flasks, using 40 cc. of Hübl solution, and allowing the action to proceed for eighteen hours in the dark, conducting care-

[1] *Loc. cit.*

ful blanks at the same time. Flash tests were made in the Elliott closed cup in the manner prescribed for the test of illuminating oils in Georgia.

Nature of sample.	Specific gravity at 15.5° C.	Iodine numbers. (1)	Iodine numbers. (2)	Flash-point. ° F.
Pure spirits of turpentine, Ware Co., Ga..	0.868	383	...	...
" " " " Calhoun Co., Ga	0.8653	388	388	...
" " " " Decatur " "	0.8695	380	375	...
" " " " (yellow), Telfair Co., Ga.....	0.8927	371	...	85
Pure spirits of turpentine, Wilcox Co., Ga.	0.8725	380	...	89
" " " " Emanuel Co., Ga	0.8668	397	...	...
Pure spirits of turpentine, Brooks Co., Ga.	0.872	384	...	...
" " " " Marianna, Fla.		364	...	87
" " " " Savannah, Ga .	0.8655	394.9	...	...
Mixture, 96 per cent. of above and 4 per cent. kerosene		383	...	...
Adulterated sample from city	0.863	373	...	83
" " " inspector, R No. 1	0.864	364	373	87
" " " " " " 2	0.8665	356	...	88
" " " " " " 3	0.8665	390.7	...	89
Wood spirits from Mobile.....	0.8625	282	...	...
" " " City Store	0.888	352	...	...
" " " Cordele	0.8605	351.9	...	...
" " " Waycross, steam process (H)	0.8725	331	...	...
Wood spirits, Waycross, steam process (R)	0.8805	298	...	...

Allen gives the specific gravity of genuine oil as ranging from 0.864 to 0.870; as is evident from an inspection of the above table, adulteration may exist and the specific gravity give no indication of it. Likewise with the flash tests; samples afterwards shown to be adulterated flashed at as high a temperature as the genuine oil. Doubtless spirits adulterated with gasoline or with kerosene, flashing at a lower point than that permitted by the Georgia law (100° F. in the Elliott cup), would respond to this test. Although I had hoped for much more decisive evidence from the iodine absorption, it becomes evident from the variations in the figures for undoubtedly genuine oil, that the process cannot be relied on for detecting small percentages of adulteration with petroleum.

Turning next to the methods of Armstrong, as given by Allen, in "Commercial Organic Analysis," second edition, Vol. II, I found the first method of distillation in a current of steam unsatis-

factory and leaving the mind in doubt in case of small percentages of adulteration. I found his method for detection of petroleum naphtha, by polymerization with sulphuric acid followed by steam distillation, better, even for kerosene, but time-consuming and tedious, and permitting adulterations of 5 per cent. and under, of kerosene, to escape detection. I had no difficulty in detecting 10 per cent. adulteration by his method, but in the case of a 4 per cent. mixture I failed utterly to discover it. In this latter case the final volume of the distillate amounted to just 4 per cent., or entirely within the limits for genuine oil, as given by Allen for pure spirits in his description of the method. Moreover, the final product could not be positively identified, as the process had destroyed the characteristic fluorescence of the petroleum, even when dissolved in ether. At this point it occurred to me to test the refractive index of the oils resulting from the steam distillation and polymerization. Obtaining important results from this procedure, after much labor and experiment the following comparatively easy and rapid method of detecting petroleum was worked out:

Transfer 100 cc. of the oil to a 600 cc. flask, preferably of Jena glass, add 50 cc. of concentrated sulphuric acid from a graduate, a few cubic centimeters at a time, agitating the acid thoroughly with the oil and cooling in a current or basin of water, if the action is very violent, between each addition of acid. When all the acid has been added and there is no further rise of temperature on repeated agitation, add 25 cc. of water to the flask, connect the flask by means of a double-bored cork and a suitable bulb-tube with a Liebig condenser and also with a large flask containing water. A current of live steam is now sent through the mixed oils and acid in the flask at such a rate as not to project any of the dark oils into the bulb-tube intervening between the flask and condenser. Distil until the volume of distillate (mixed water and oil) reaches 100 cc., now separate the oil from the water and test with a few drops the refractive index, then measure the oil approximately, transfer to a small dry flask of 50 cc. capacity, glass-stoppered, and add as much fuming sulphuric acid as there was of oil, agitate violently, removing the stopper occasionally for the escape of sulphur gases. Pour the resulting mixture into cold water, separate the oil which floats, transfer it to a distilling flask and repeat the distillation in a current of steam. Distil to a

volume of 100 cc., separate the oil from the water as before, take the refractive index, then polymerize the resulting oil for the third time with at least an equal volume or better, twice its volume of fuming sulphuric acid. The resulting mixture is again poured into cold water, the oil separated and washed with cold water, its volume noted and the refractive index again taken. The instrument used in taking the refractive indices was the "Zeiss butyro-refractometer," provided with a centesimal scale, ranging from N_D 1.42 to 1.49. For the sake of convenience and greater distinctiveness the results given below are expressed in terms of the centesimal scale of the butyro-refractometer. These may be translated into corresponding refractive indices by means of the table given on page 342, Volume III, of Wiley's "Principles and Practice of Agricultural Analysis." All readings were made at a temperature of 25° C. and by sodium light.

Nature of sample.	Oil from 1st polymerization.	Oil from 2nd polymerization.	Oil from 3rd polymerization.	Final vol. cc.
Calhoun Co., turpentine	79	58	33.5	1.1
Decatur Co., "	74	48	32.0	1.2
Savannah pure spirits	82	58	35.0	0.7
Pure spirits with 1 per cent. kerosene	72	43	25.0	1.4
" " " 2 " " "	65	39	21.0	2.2
" " " 4 " " "	57	34	18.0	2.7
Adulterated samples from inspector R, No. 1	49	17	13.0	3.5
" " " " " " 2	70	45	20.0	2.1
" " " " " " 3	71	43	22.0	2.0
5 cc. of pure kerosene	18	..	12.0	2.9
Wood spirits, Cordele	80	66	43.0	2.0
" " crude	79	64	31.0	1.7
" " steam process	69	45	30.0	1.8
" " Mobile	78	64	37.0	2.0

In no case was I able to reduce the reading below 30 with genuine turpentines or wood spirits, but with adulterated spirits, containing even as little as 1 per cent. of kerosene, the reading fell as low as 25 on the third polymerization, and could be slowly reduced to 22 by continued treatment with fuming acid; the greater the percentage of adulteration the lower in the scale would the reading fall.

I have not succeeded yet in making the method quantitative, though the chemist would run but little risk in certifying the final volume to be the minimum percentage of petroleum, when the

refractometer reading is as low as 22. Adulteration with naphtha or kerosene with low flash-point would show still lower readings than those obtained above. The kerosene sold in this state flashes at or above 100° F. in the Elliott cup; it is, therefore, to be expected that adulteration with kerosene of a lower flash-point would show a somewhat lower reading. Adulteration with rosin spirits may be shown by the Liebermann-Storch test.

Adulteration with wood spirits is unlikely, since there is but little difference in price between wood and genuine spirits. The crude wood spirits may be known by its odor, but with a highly refined article it would be different. Adulteration of this kind may be detected as follows: Kerosene or naphtha having been proved to be absent by the above process of polymerization, a distillation is carried out on 100 cc. of the sample in a flask made precisely according to the specifications of Engler for the distillation of illuminating oil.

The flame used must be small, the thermometer rise very slowly, and the first 0.5 cc. of distillate collected by itself, drop by drop, and the refractive index taken at 25° C. In the case of no genuine oil will this fall below 60, being usually 61 to 63. Several samples of wood spirits show readings as low as 59, 58 and even 57. When the wood spirits do not show a low initial reading, they nearly always show a high reading on the final portion of the distillate. I have adopted the 97th and 98th cc. of the distillate as being in practice the most convenient to collect separately for the purpose of taking the final refractive index. In the case of genuine spirits this reading will not exceed 77, usually much less, but with wood spirits will (especially if the initial reading be high) exceed 77 and may even reach 90. A further distinction between genuine and wood spirits may be observed during this distillation; in nearly all genuine spirits 95 per cent. will have distilled over by the time the temperature reaches 165° C., whereas, with wood spirits, when 95 per cent. have come over, the thermometer is much higher than 165°. It is possible that the methods described above may, with modifications, be applied to the detection of turpentine in the more costly essential oils. I have to thank Messrs. Williams and Burton, of this laboratory, for their indispensable aid and valuable suggestions during the progress of the work.

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SOME NOTES ON LAURENT POLARISCOPE READINGS.[1]

By Geo. W. Rolfe and Chas. Field, 3rd.

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For many years the Laurent polariscope has been the common instrument in our chemical laboratories for the measurement of optical rotation, especially in the determination of specific rotatory powers, which are the constants of calculation in polarimetric analysis.

Till comparatively recently the results obtained with the Laurent polariscopes have been accepted as expressing rotations of the plane of polarization of the D ray, or ray of standard wave-length. The light used in Laurent measurements, as is well known, is made by vaporizing common salt in a powerful Bunsen burner, and filtering the rays through a section of potassium bichromate crystal.

The *saccharimetric* scale of the Laurent polariscope is based on the *specific rotation of quartz*, which was taken as 21.667 at the standard temperature. Later measurements of the specific rotation of quartz, even some of more than twenty years ago, give a higher value—21.72 at 20°. As by common usage, the 100-point of the Laurent saccharimeter is a fixed one, equivalent to the rotation value of 21.667, an attempt has been made to reconcile this value to the original definition by stating that this expresses the rotation of quartz at 6°. Obviously, this is merely a matter of definition, the scale being based on a fixed rotation, independently of whether this be the specific rotation of quartz or not.

The Laurent instrument is little used for saccharimetry in this country, the value of the specific rotation of quartz given by the instrument being chiefly of interest as a point of reference for determining the accuracy of its measurements as expressing angular rotations of the plane of polarization of the standard yellow ray.

In 1890[2] Lippich published a paper designed to prove, theoretically, that errors of 0.2 per cent. or more necessarily existed in Laurent measurements. As confirmation of this, in the same paper, Lippich also published comparative measurements of the optical rotation of a standard quartz plate made on a Lippich polariscope and two of the Laurent type, the readings of which latter showed variations of forty-five to eighty-two seconds from those of the Lippich polariscope. It should be noted that, in these

[1] Read at the Providence meeting of the American Chemical Society.

[2] "Zur Theorie der Halbschattenpolarimeter," *Wien Sitzungsber* [II], **99**, 695.

experiments, Lippich filtered the sodium light through both potassium bichromate and cupric chloride solutions, so that the light he used probably differed appreciably from that designed for the Laurent polariscope.

Landolt[1] has pointed out that the sodium light as usually employed in polariscopic measurements is not homogeneous, but is made up of light of many wave-lengths, most of them differing slightly from each other, but that such light can be considered as homogeneous light which has a wave-length of the ray which is the resultant in intensity of all the rays emitted. This ray is termed the "*optical center*"[2] of the light. In his work on optical rotation, Landolt discusses the different optical centers of light used in polarimetric measurements, but does not consider exactly the kind of light used by Laurent instruments.

In most of the more recent accepted measurements of the specific rotation of quartz the light used has been the yellow rays of the two D lines of the spectrum, separated by spectroscopic methods, either from white light or from sodium flame.

For the Lippich polariscopes, Lippich has designed a ray filter which practically absorbs all light except those rays adjacent to the D lines. This filter purifies the light of incandescent sodium chloride vapor so that its optical center is practically that of the spectrally purified light. According to Landolt, who describes the preparation of the solutions in detail, it consists of a 10-cm. absorption cell filled with a 6 per cent. solution of potassium bichromate and a 1.5 cm. cell filled with a specially prepared solution of uranyl sulphate.[3]

Consideration of many published rotation values obtained on Laurent polariscopes, as well as readings of the two instruments of the sugar laboratory of the Massachusetts Institute of Technology, has led us to believe that polariscopes of this type, if of French make, give readings which are concordant within one minute at least, although about 0.2 per cent. lower than those obtained with the Lippich ray filter. As long ago as 1899 one of us published this opinion.[4]

Quite recently we have made two series of rotation measurements of two standard quartz plates on a Laurent polariscope,

[1] "Optische Drehungsvermögen," p. 360.
[2] "Optischer Schwerpunkt."
[3] Lippich: *Ztschr. für Instr.*, **12**, 340; Landolt: "Optische Drehungsvermögen," p. 362.
[4] This Journal, **21**, R105 (1899).

one set with the light designed to be used by the Laurent polariscope, sodium chloride light filtered through a section of bichromate crystal; the other set, with sodium chloride light passed through a Lippich ray-filter. The instrument used was a Laurent, "large model" made about 1888 by Leon Laurent, of Paris.

The table gives the result of the measurements as well as the saccharimetric readings of the two quartz plates, on the saccharimeters of the Institute laboratory, which are graduated in the standard Ventzke scale for use of Mohr flasks, and their readings also on a triple-shade saccharimeter of the United States Department of Agriculture, which latter readings were made by Dr. Wiley in 1898, and obviously are on the true cubic centimeter scale.

The saccharimetric readings of "Quartz A" plate show that, within a small error, it is a millimeter in thickness.[1] On this account it is interesting to note that the value given with the ordinary light used with the Laurent polariscope is practically that obtained for the specific rotation of quartz by the *earlier* investigators, while that given by the Lippich light closely approximates to the *modern* value.[2] The results, as a whole, have led us to believe that the difference in values obtained by the Lippich and Laurent measurements are not due to the imperfections of the Laurent instrument, but to the kind of light used, at least up to the precision required in chemical laboratory measurements, or 0.1 per cent. of the values obtained.

The greater convenience of the Laurent polariscope, owing to its end-point adjustment being independent of the position of the polarizer for the regulation of the light intensity, as well as the advantage of the bichromate section over the Lippich ray-filter, which absorbs a large percentage of light and soon deteriorates, owing to the oxidation of the uranium solution, makes the Laurent more advantageous than the Lippich for general laboratory measurements. Our results show that Laurent measurements can be converted to the standard of spectrally purified light by increasing their value 0.2 per cent. The tabulated light factors calculated from the different rotation and saccharimetric values

[1] Landolt: Optische Drehungsvermögen" (First Edition), p. 162. The plate was always placed in the instruments in a definite axial position, but we have been unable to detect any difference in its readings in different positions.

[2] Landolt: "Optische Drehungsvermögen," p. 130.

will, it is hoped, explain some of the different values which are given indiscriminately, and, in fact, without proper explanation in the various publications dealing with optical rotation.

It may be unnecessary to point out that Rimbach,[1] Landolt,[2] and others have shown that the light factor of a quartz-wedge saccharimeter may vary with the nature of the substance measured. This is on account of the difference in the rotary dispersion of quartz and the solution measured, the result being that all the rays of the spectrum whose planes are rotated by the solution are not restored exactly to their original angular positions by a section of oppositely rotating quartz of one definite thickness. Hence no position of the quartz compensation wedges will exactly restore the original light effect of the end-point when the solution is placed in the instrument, and a more or less parti-colored field is given in shadow saccharimeters. If the dispersion difference is slight, this can be obviated and an evenly tinted field obtained by absorbing the rays of the blue end of the spectrum by means of a ray filter of bichromate solution, or somewhat less effectively, but more conveniently by means of a piece of brown (carbon) tinted glass. The ray filter, however, in the case of the quartz-wedge saccharimeter, merely assists in obtaining a more precise end-point. The light factor, as determined by a solution of commercial glucose, for instance, will differ appreciably from that obtained with quartz. Even cane-sugar solutions differ sufficiently from quartz in rotary dispersion to give light factors of slightly different value.

Hence, it is imperative, in stating that the light factor of a saccharimeter is a certain value, that reference should be made (1) to the exact nature of the light used in the rotation readings; (2) the saccharimetric standard of the scale of the quartz-wedge instrument; (3) the nature of the substance measured; and (4), obviously, the temperature at which the comparisons are made. It would seem as if these conditions of measurement ought to be well known, but they are singularly ignored in statements in publications on the subject, to the confusion of most readers.

READINGS AT 20°.

	(1) Sacch. readings, orig. Ventzke scale.	(2) Sacch. readings, true cc. scale.	(3) Laurent readings, orig. light.	(4) Laurent readings, Lippich Ray-filter.
Quartz A	62.66	62.45	21.667	21.719
Quartz D	96.02	95.77	33.200	33.284

[1] *Ber. d. chem. Ges.*, **27**, 2282
[2] *Ibid.*, **21**, 191.

CALCULATED LIGHT FACTORS.

	From (1) and (3).	From (1) and (4).	From (2) and (3).	From (2) and (4).
Quartz A	0.3458	0.3466	0.3469	0.3478
Quartz D	0.3458	0.3466	0.3467	0.3475

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VARIATIONS OF STANDARD AMONG VENTZKE SACCHARIMETERS.[1]

BY HARRIS E. SAWYER.

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IT SEEMS generally to be supposed that the Ventzke saccharimeter is always standardized to read 100° on a 200 mm. column of a solution, prepared and polarized at 17.5° C., of 26.048 grams of sucrose, weighed in air, in 100 Mohr cubic centimeters. Rolfe has claimed,[2] however, that through most instruments now in use conform to this standard, certain of newer saccharimeters are graduated for the slightly stronger sugar solution produced by dissolving the old normal weight in 100 cubic centimeters; and in view of this claim it seemed advisable to the writer to ascertain what standard was adopted in the graduation of his own instrument—a Schmidt & Haensch triple-field, No. 4914—purchased about three years ago.

To this end he first polarized with great care a series of four positive quartz plates belonging to the Massachusetts Institute of Technology. These plates, which read respectively 55.30°, 62.66°, 95.99° and 100.07° on the two half-shadow instruments of the Institute,[3] gave the values 55.08°, 62.45°, 95.75° and 99.86° on the writer's instrument, the mean ratio between the two sets of values being 1.0028, whereas the theoretical ratio should be 1.0023 in case the instruments were graduated respectively for Mohr and for true cubic centimeters. Since the Institute's instruments are known to be adjusted to the Mohr cubic centimeter standard, it seemed obvious that the writer's must be intended for use with true cubic centimeter flasks. At this point, therefore, he communicated his observations to Schmidt and Haensch, in-

[1] Read at the Providence meeting of the American Chemical Society.

[2] Review Am. Chem. Research, V, 105 (1899); This Journal, **25**, 1007 (1903).

[3] The foregoing values are the means of the values given for the instruments No. 2880, Schmidt and Haensch, and No. 624, Scheibler, in the tabulation on p. 994.

quiring if this was not the case; and in due time he received their answer that "the saccharimeter, No. 4914, as all our quartz wedge polariscopes, has been graduated for the old scale—26.048 grams weighed in air with brass weights, 100 Mohr cubic centimeters, 17.5° C." In view of this reply the writer found it advisable to carry his investigation further.

It was necessary first to determine, by tests with pure sugar, what concentration of solution would, at 17.5° C., give a reading of 100° on the saccharimeter in question. Accordingly, a set of weights, a 200 mm. polariscope tube and a tenth-degree thermometer were submitted to the Bureau of Standards for correction; a sample of pure sucrose, prepared by the method of the International Commission and checked by Dr. Wiley against a pure sucrose prepared by Herzfeld, was obtained from the Bureau of Chemistry; a true 100 cc. flask, graduated by the United States Coast and Geodetic Survey, was recalibrated and found to contain within 0.01 per cent. of its indicated capacity at 17.5°; and also, since the neck of this flask was somewhat wide and its graduation mark at a distance from the bulb, another flask with a neck only 8 mm. in diameter was provided with a mark 5 mm. above the beginning of the cylindrical portion, and was calibrated with great care, being found to contain 98.18 true cubic centimeters at the temperature of the subsequent determination.

After preliminary trials, to acquire manipulative facility, two determinations of the sugar value of the saccharimeter were made.

(1) One hundred true cubic centimeter flask; 26.048 grams pure sucrose; temperature of air and solution at time of preparation and polarization, 24° C.; mean of 10 zero-point readings, —0.204°; mean of ten polarizations, 99.601°; net observed polarization, 99.805°.

(2) 98.18 true cubic centimeter flask; 25.509 grams pure sucrose; temperature of air and solution at time of preparation and polarization, 28° C.; mean of ten zero-point readings, —0.008°; mean of ten polarizations, 99.395°; net observed polarization, 99.403°.

In calculating the result of the first determination, 0.02 per cent. was allowed for the expansion of the 100 cc. flask between 17.5°, the temperature of calibration, and 24°. The polariscope tube employed has, at 17.5°, a length of 200.01 mm., corresponding

to 200.02 mm. at 24°, and to 200.03 mm. at 28°; and though the excess of length is very slight, it nevertheless was taken into account in the calculations.

In reducing the polarizations from 24° and 28°, the temperatures of observation, to the standard temperature of 17.5°, the factor 0.0317° V. = 1.0° C. was employed, this being the mean of the values given by the United States Coast and Geodetic Survey, Andrews, Landolt, and Wiley,[1] and in almost absolute agreement with the result of the latter investigator.

All these corrections for temperature having been applied, the values 100.00° and 99.72° were obtained, as indicating the polarizations of the writer's sugar solutions at 17.5° in a 200 mm. tube. Since the solution used in the first determination was prepared to contain 26.048 grams of sucrose in 100 true cubic centimeters, no further correction of the value 100° is necessary. In the second determination, however, the solution was of less than normal concentration, since 25.509 grams in 98.18 cc. corresponds to 25.981 grams in 100 cc. Accordingly, the value 99.72°, obtained as above in the second determination, was multiplied by $\frac{26.048}{25.981}$; and the value 99.98° was thus obtained as representing for this determination, the polarization of a solution of 26.048 grams of sucrose in 100 true cubic centimeters at 17.5°. It was thereby established that the writer's saccharimeter is, indeed, adjusted to the true cubic centimeter standard.

It now remained to be seen whether the difference between the standard of this instrument and that of those at the Institute of Technology seemed to be due to intent or to such calibration errors as may affect all graduated apparatus. That they could be due to the latter cause seemed wholly incredible, since the mean difference of the quartz plate values amounted to 0.28 per cent., whereas Landolt[2] has stated that variations in the 100° point of Schmidt and Haensch saccharimeters do not commonly amount to more than from 0.05°-0.10° V. and that they usually are smaller. Accordingly, an examination of all the compensation saccharimeters in Boston was undertaken, by means of the quartz plates already mentioned, in the hope of getting light upon this question. It was presumed that chance variations of standard would result in values for the

[1] This Journal, **21**, 584 (1899).

[2] Landolt-Long: "Optical Rotation of Organic Substances," p. 375.

readings of the plates, which would be scattered irregularly between, and possibly beyond, those already obtained, and that the intentional existence of a double standard of graduation would be shown by the readings falling into two groups, the values within each group approximating those already given, and differing among themselves by such small amounts as Landolt's statement would lead one to expect.

It is well known to polariscopists that, in consequence of the variation of the specific rotary power of quartz with changing temperature, it is necessary to leave plates and wedge-compensations to come to temperature-equilibrium, if concordant results are to be obtained in such an examination as is here described. Accordingly, the greatest possible care was taken to maintain such equilibrium during all of the writer's observations; and no results are included in the following tabulation save those which are considered to be essentially free of temperature error.

The number of observations made upon any individual instrument has varied according to circumstances. In general, any value given in the table represents from 5 to 10 zero-point readings and as many polarizations; in many cases a single value represents from 25 to 30 such readings, and in some cases from 50 to 60.

On the writer's own instrument many series of readings were made with almost identical results; thus, on the A plate the means of three series, taken at intervals of several weeks, were respectively 62.44°, 62.45° and 62.46°, the probable error of each mean being ±0.02°. On other instruments of the same type—Lippich polarizer, triple field—fewer readings were made, but on account of the great sensitiveness of these modern polariscopes the mean errors were not perceptibly greater. With the older half-shade instruments, having the Jellet polarizer, the mean errors were slightly greater, amounting to ±0.03° or 0.04°; and with the color instruments examined, the mean errors affecting the tabulated results are in the vicinity of ±0.06° to 0.08°; but with the latter instruments great patience was required to attain such a degree of accuracy in reading.

It is now obvious, on consideration of the tabulated values, that the saccharimeters examined by the writer must be grouped in two classes.

COMPARISON OF QUARTZ WEDGE SACCHARIMETERS.

Maker.	Type.	Serial No.	C Plate.	A plate.	D plate.	E plate.
S and H	color	1159	....	62.46	95.68	99.85
"	"	1435	55.09	62.49	95.78	99.83
"	half shade J..	3258	....	62.40	....	99.80
"	" " "..	3443	....	62.36	....	99.76
"	" " L..	3010	....	62.50	....	99.85
"	" " "..	3041	....	62.48	....	....
"	" " "..	4720	....	62.45	....	99.87
"	" " "..	4914	55.08	62.45	95.75	99.86
"	" " "..	5045	....	62.52	...	99.88
"	" " "..	3923	55.11	62.45	95.77	99.84
"	" " "..	5862	....	62.47	....	99.83
"	color	1885	....	62.68	....	100.09
"	half shade J..	2540	....	62.68	....	100.11
"	" " "..	2880	55.32	62.66	96.02	100.06
Scheibler	" " "..	624	55.28	62.66	95.96	100.08
Peters	" " "..	103199	....	62.61	....	100.03

J signifies Jellet polarizer.
L " Lippich polarizer.

Taking as the basis of comparison the values of the E plate, which are nearest the 100° point, we see that the two older color instruments and the modern shadow instruments of Schmidt and Haensch must be classed together—the lowest value being 99.76°, the highest 99.88°, and the mean 99.837°. In a second class are included one of the later Schmidt and Haensch color instruments and two of their earlier half-shades, together with an old Scheibler and a modern Peters. The values of the plate on these instruments range from 100.03° to 100.11°, the mean being 100.076°. The ratio between these means is 1.0024, instead of 1.0023, as required by theory between instruments graduated for the Mohr and for the true cubic centimeter.[1]

[1] The writer calls attention to the fact that while the mean E plate values for the two classes of saccharimeters are separated by an interval of 0.24° V. and show the ratio 1.0024, the interval between the mean A plate values 62.46 and 62.66 is 0.20°, and the ratio 1.0032. Strict proportionality would demand that the latter interval should be slightly less, and the ratio lower. That this is not the case, has no bearing on the subject of this communication, since the standard of the saccharimeter is determined by the value of the 100° point of its scale. Indeed, the introduction of the values of the lower plates in the foregoing tabulation is non-essential, although they have a certain confirmatory value. But while this is the case and while some variations from proportionality are to be expected throughout every scale, the fact that many instruments show divergences in the same direction is worthy of note and may have some significance. Accordingly, the values of the lower plates are given, so far as they have been determined ; and a study of their relations to the E plate values is being carried forward.

If, now, it be granted that the difference between the saccharimeters of these two classes is intentional—that certain of them were meant to be used with sugar solutions prepared in Mohr cubic centimeter flasks, and the others in conjunction with true cubic centimeter flasks—the writer's observations agree entirely with Landolt's statements. In the one class the extreme variation in the readings of the E plate on ten saccharimeters is 0.12° V.; in the other class, including five instruments, it is still smaller, only 0.08°.

If, on the other hand, it be denied that the instruments were graduated for two distinct standards, Schmidt and Haensch are confronted by an extreme variation of 0.35° V. at the 100° point among thirteen of their instruments—a variation far greater than any careful instrument-maker would ever have permitted. And furthermore, we have to explain the fact that between the readings of instruments Nos. 5045 and 2880, respectively 99.88° and 100.06°, there is a gap of 0.18°, to bridge which no instrument has been found.

It seems, therefore, as if there must exist a double standard of graduation among the saccharimeters of Schmidt and Haensch;—as if their earlier instruments were graduated for the true cubic centimeter, as if in time this standard had been abandoned for the more convenient and more popular Mohr cubic centimeter, and finally, as if the latter in turn had been abandoned in consideration of the growing feeling against the double standard of graduation for volumetric flasks. In view of the fact that 0.23 per cent. may make, at times, a material difference in the results of a saccharimetric determination, it seems desirable that the attention of chemists should be called to the foregoing facts.

244 COLUMBIA ROAD, DORCHESTER, MASS.

THE ANALYSIS OF PORTLAND CEMENT.

BY BERTRAM BLOUNT.

Received May 16, 1904.

A YEAR or two ago the New York Section of the Society of Chemical Industry suggested the establishment of a standard method for the analysis of Portland cement. Samples of cement were distributed to various chemists to be analyzed according to

a method laid down by the committee. Dr. Hillebrand was good enough to undertake the analysis of these samples as a control. In May, 1902, I read a paper before the New York Section of the Society of Chemical Industry in which I demurred to the methods proposed by the committee on two chief grounds: (*a*) That standardization of strictly analytical processes was undesirable; and (*b*) that the methods proposed by the committee were erroneous.

In the course of this controversy I had the advantage of meeting and conferring with Dr. Hillebrand, and on many of the points which appeared to be at issue between us we found ourselves in substantial agreement. Dr. Hillebrand, in a paper lately read before the American Chemical Society,[1] has quite frankly intimated his concurrence. There remain a few matters of great moment to the manufacturers and users of Portland cement and to the chemists who control the quality of their output, which are still in doubt; as the question affects a large industry and is of much analytical interest it may be usefully discussed in detail.

Before passing to these matters it may be said that the inaccuracies occurring in the analyses of some of the chemists who examined the samples distributed by the committee, are so numerous and serious as to show that the training, skill and care of the operators are inadequate; this state of things calls loudly for a remedy; the provision of such a remedy appears to be of more pressing importance than the erection of a standard method of analysis.

One of the principal questions as to the proper method of analyzing Portland cement is that of the determination of its insoluble residue. The samples analyzed by Dr. Hillebrand and reported on in his paper appearing in this Journal, November, 1903, contained so little that it could reasonably be ignored. But usually the proportion is substantial, ranging from 0.5 to 1.5 per cent. in a properly mixed and burnt cement and exceeding the latter figure in one which has been poorly prepared. The determination of insoluble residue is of value because the figure obtained is an index of the care which has been used in manufacture; a cement containing 5 per cent. of added sand would be diluted to that extent only, whereas one containing 5 per cent.

[1] This Journal, **25**, 1180.

of insoluble residue is not merely diluted, but has incontestably been badly made. The method which I devised and have used for nearly twenty years consists in dissolving the cement in hydrochloric acid, evaporating the solution to dryness, but not intentionally baking the evaporated material, re-dissolving in hydrochloric acid, filtering, washing, dissolving out the precipitated silica with sodium carbonate solution and collecting the final insoluble residue. It may be fairly assumed that a silicious residue, which has resisted this series of treatments, is inert and valueless as a cementitious material. I believe that I am not misinterpreting Dr. Hillebrand when I say that he agrees with this; but he goes further and suggests that the treatment is too drastic and that it would be better to determine the insoluble residue in such a way that it is not exposed to digestion with strong hydrochloric acid. The method he proposes is to dissolve in dilute hydrochloric acid, filter at once and to remove any precipitated silica by means of sodium carbonate. This suggestion is important and has been examined in the following maner. Four samples of cement were chosen and the insoluble residue determined in each, both by the method which Dr. Hillebrand has proposed and that which I ordinarily use. My analyses of these cements are as follows:

	1. Per cent.	2.[1] Per cent.	3. Per cent.	4. Per cent.
Silica (SiO_2)	21.90	16.64	22.26	21.18
Insoluble residue	1.12	1.62	1.32	0.52
Ferric oxide (Fe_2O_3) and Alumina (Al_2O_3)	10.66	10.20	11.20	10.14
Lime (CaO)	61.66	62.90	61.68	63.86
Magnesia (MgO)	1.33	1.47	1.14	1.27
Sulphuric anhydride (SO_3)	1.08	1.58	1.10	1.10
Carbonic anhydride (CO_2)	1.40	3.05	0.70	1.02
Water (H_2O)		1.13		
Sulphur	...	0.08	...	...
		98.67		
Deduct oxygen equivalent to sulphur	...	0.04	....	....
	99.15	98.63	99.40	99.09
Alkalies and loss	0.85	1.37	0.60	0.91

Duplicate determinations of the insoluble residue in each were made by Dr. Hillebrand's method and my own:

[1] Cement No. 2 is adulterated with limestone.

	Dr. Hillebrand.		Bertram Blount.	
	Per cent.	Per cent.	Per cent.	Per cent.
(1).....	3.48	3.28	1.10	1.16
(2).....	3.34	3.12	1.60	1.64
(3).....	5.20	5.00	1.28	1.36
(4).....	0.80	0.96	0.50	0.54

The results are fairly concordant for methods of this kind and show that both processes can be relied upon to yield consistent results. As might be expected, the difference between the two modes of procedure has led to their values differing widely. If we assume with Dr. Hillebrand that the insoluble residue obtained by his method is inert, evidently the determination of this material is of even greater importance than had been supposed; it is, however, not easy to obtain conclusive evidence on this point. The state of subdivision of the particles comprising cement has a great influence on their activity; unground clinker is scarcely more cementitions than so much limestone. Moderately fine particles, on the other hand, though setting slowly, will set eventually and it would be rash to assume that a material, apparently inert when tested for the short periods of time generally available in laboratory experiments, will not prove itself active at long dates, and in practice contribute to the strength of the concrete or mortar prepared with it. Bearing this in mind, one is not surprised to find that the insoluble residue obtained by Dr. Hillebrand's method is a cementitious material. This fact was ascertained in the following way: The insoluble matter from cement No. 1, isolated strictly according to Dr. Hillebrand's prescription, was finely ground and then treated again by Dr. Hillebrand's own method. The final insoluble residue thus obtained was 1.52 per cent. and 1.66 per cent. in duplicate experiments, as against a previous mean value of 3.38 per cent. on the unground substance. In point of fact the re-treatment reduces the insoluble residue to something closely approaching that found by my method of analysis, which, on the same cement, gave 1.10 per cent and 1.16 per cent. insoluble residue. It would appear from this that the chief difference between the two methods arises from the necessity of more finely grinding the cement if dilute acid is to be used; when fine grinding is substituted for the use of strong acid, similar results are obtained.

The nature of the insoluble residue, prepared by Dr. Hillebrand's method, was investigated. Two samples from cement No. 1 were analyzed, giving the following figures:

	Per cent.	Per cent.
Insoluble silicious matter	61.48	69.25
SiO_2	8.69	7.90
Al_2O_3 and Fe_2O_3	13.32	10.84
CaO	12.99	8.49
MgO	0.82	1.35
Alkalies and loss	2.70	2.17
	100.00	100.00

The samples are similar in composition. Such differences as ...ey exhibit are not greater than might be expected, considering that the method of isolation is arbitrary and that small variations of condition will certainly influence the nature and extent of the decomposition of moderately refractory silicates.

From a study of these figures I thought it possible that this insoluble matter might be cementitious. Accordingly, a fairly large quantity of the material (about 25 grams) was isolated. This was ground and gauged with water in the manner of a cement. As might be predicted, it set feebly; it is, in fact, not a cement *per se*, but rather a puzzuolanic material. Its activity as a puzzuolana was proved by gauging it with one-third of its weight of quicklime; it set to a hard mass. As there is always an abundant quantity of lime set free from the decomposition of calcium silicates and aluminates in the process of the setting of cement, capable of acting with a puzzuolanic material, I conclude that the insoluble matter, isolated by Dr. Hillebrand's method, is not inert, but belongs in great part to the cement itself. The insoluble residue isolated by my own method is almost wholly silica in rather coarse fragments and is substantially inert. On these grounds I prefer my original method for determining insoluble residue.

Next, with regard to the determination of silica in cement, Dr. Hillebrand has done excellent service in promoting accuracy in mineral analysis by insisting on the necessity of a double evaporation. I agree that this double evaporation is necessary when the silica is set free in a mass of material such as is produced when a silicate is fused with sodium carbonate and the melt is

decomposed with hydrochloric acid, but I consider that it is not requisite when the total quantity of material handled is small and the whole is well baked. It is perfectly practicable to obtain substantially the whole of the silica from Portland cement by a single evaporation.

Using the four cements, analyses of which are given below, the following figures were obtained, the correction for the small amount of matter other than silica being given in each case; the quantity of cement used was 0.5 gram.

Sample.	Total residue chiefly silica obtained by second evaporation.	Matter other than SiO_2 contained in this residue.	Actual SiO_2.
1 (*a*)	0.0010	0.0001	0.0009
(*b*)	0.0012	0.0002	0.0010
2 (*a*)	0.0012	0.0002	0.0010
(*b*)	0.0008	0.0001	0.0007
3 (*a*)	0.0016	0.0002	0.0014
(*b*)	0.0014	0.0002	0.0012
4 Porcelain (*a*) ...	0.0015	0.0002	0.0013
(*b*) ...	0.0016	0.0002	0.0014
Platinum (*a*)	0.0009	0.0002	0.0007
(*b*) ...	0.0010	0.0003	0.0007

The first three samples were evaporated in porcelain; Sample 4 was treated in both porcelain and platinum. It will be seen that even the largest of these quantities (0.0016 gram, equivalent to 0.32 per cent.) is insignificant and will in no way influence the opinion of the chemist on the quality of the cement analyzed. There is also ground for believing that a good part of the silica obtained by a second evaporation is of extraneous origin and is not derived from the cement. The lower result for Sample 4, which was treated in platinum, points this way, and evidence more direct than this is available. The filtrate from the second evaporation of Sample 4 was evaporated, filtered, and the process repeated until in all seven such operations had been performed. The experiment was made in duplicate and its results are instructive.

It is perfectly clear that a considerable part of the small quantity of silica, obtained by a second evaporation, is derived, not from the cement itself, but from the vessels used and from inevitable dust; when correction is made for this, the quantity of silica retrieved by a second evaporation properly conducted becomes negligible, certainly not more than 1 mg.

SAMPLE 4.

		Series A.		Series B.	
			containing matter other than SiO_2.		containing matter other than SiO_2.
		Gram.	Gram.	Gram.	Gram.
SiO_2 + insoluble residue	Evap. 1.....	0.1073	.....	0.1075	.....
	" 2.....	0.0015	0.0002	0.0016	0.0002
	" 3.....	0.0006	0.0002	0.0007	0.0003
	" 4.....	0.0006	0.0002	0.0006	0.0001
	" 5.....	0.0004	0.0001	0.0005	0.0001
	" 6.....	0.0005	0.0001	0.0005	0.0002
	" 7.....	0.0004	0.0001	0.0005	0.0002

The next matter in which there is a difference of view between Dr. Hillebrand and myself is whether silica, separated by the ordinary process of solution and evaporation, is pure or contains entangled in or associated with it sensible quantities of alumina and other bases. To examine this question I chose a cement (No. 4 of the series given above) containing a very small quantity of insoluble residue (*viz.*, 0.52 per cent.). In this insoluble residue there was almost nothing but silica; hence, any alumina or other metallic oxides found in the silica + insoluble residue, isolated from the cement in the ordinary process of analysis, must be derived from the cement itself. This cement was analyzed in the usual way, the silica and insoluble residue separated and treated with hydrofluoric acid. The total weight of matter other than silica in four successive determinations is stated below; for comparison, the quantity of matter other than silica found in the insoluble residue is also given.

ON 0.5 GRAM.

Matter other than silica in insoluble residue. Gram.	Matter other than silica in total silica + insoluble residue. Gram.
0.0008	0.0007
.....	0.0005
.....	0.0005
.....	0.0006

It is evident that when the solution, evaporation and resolution of the cement are properly conducted, no alumina remains with the silica except that which is present in the insoluble residue.

One other point of some importance may be dealt with, namely, the possible presence of silica in the precipitate of ferric oxide and alumina. Dr. Hillebrand's view is that silica, remaining in

the filtrate from a single evaporation for that substance, will appear in the ammonia precipitate in sensible amount; he also holds that the figures which I have previously advanced may not represent the whole of the silica present in the ammonia precipitate. To determine this question, experiments were made on the same four cements previously employed. The ammonia precipitate obtained after a single evaporation for silica and without special precaution of any kind, was analyzed for silica by the method of fusion with bisulphate, proposed by Dr. Hillebrand. The only deviation consisted in the addition of hydrochloric acid after evaporation with sulphuric acid to hasten the solution of aluminum sulphate. The quantity of cement used in each case was 0.5 gram and the experiments were made in duplicate, the evaporations being performed both in porcelain and platinum. The results are as follows:

	Sample 1.		Sample 2.		Sample 3.		Sample 4.	
	In porcelain.	In platinum.	In porcelain.	In platinum.	In porcelain.	In platinum.	In porcelain.	In platinum.
Total matter recovered	0.0017	0.0015	0.0018	0.0015	0.0021	0.0017	0.0017	0.0011
Matter other than SiO_2	0.0003	0.0002	0.0004	0.000	0.00063	0.0003	0.0004	0.0001
Silica from $KHSO_4$ ..	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008
Actual SiO_2 contained in the NH_3 precipit'e	0.0006	0.0005	0.0006	0.0004	0.0007	0.0006	0.0005	0.0002

It is evident, therefore, that the amount of silica contained in the ammonia precipitate from cement, analyzed in the customary manner and with only one evaporation for silica, is negligibly small.

Certain deductions may be drawn from the data given above and from those previously published.

Experiment has shown that in the analysis of cement, silica can be separated by a single evaporation with a maximum error of 0.32 per cent. and that this error is usually smaller; that the amount of silica appearing with the ferric oxide and alumina will not exceed 0.14 per cent., and is generally less; that a single precipitation suffices for the separation of ferric oxide and alumina from lime and of lime from magnesia.

I venture to believe in the light of the foregoing facts that the method laid down in the paper read by me before the New York Section of the Society of Chemical Industry in May, 1902, is satisfactory.

If errors occur, they are due to bad work and not imperfection in the methods of analytical separation.

I desire to thank Mr. W. Woodcock for his assistance.

LONDON, ENGLAND,
May 5, 1904.

A RAPID METHOD FOR THE DETERMINATION OF LIME IN CEMENT.[1]

BY BERNARD ENRIGHT.

Received June 7, 1904.

A RAPID determination of the lime in cement, a method by which the lime content can be accurately determined, in a brief space of time, without waiting for the lengthy evaporations and dehydration of the silica present, is frequently very desirable in the manufacture of the highest grade of Portland cement. For these reasons the following method has been devised; it has been thoroughly tested and has given very satisfactory agreement with accurate lime determinations made by lengthy methods in common use.

The method of procedure is as follows: Five-tenths of a gram of a cement, as a precautionary measure repulverized in an agate mortar, is weighed out, preferably into a casserole of about 12 ounces capacity. About 100 cc. of hot water are introduced in a stream from a wash-bottle in such a manner as to keep the cement in complete suspension, about 30 cc. of hydrochloric acid (1:1) then added, the rapid agitation of the liquid being continued during its introduction. After the addition of a few drops of bromine water the solution is rapidly brought to a boil and boiled a few minutes to effect complete solution of practically everything but a few flakes of silica and to expel the bromine. Dilute ammonia is now cautiously added with constant stirring until a faint excess is present, and the solution again brought to a boil for a minute. It is then filtered, preferably on an 11 cm. filter-paper,

[1] Read before the Lehigh Valley Section of the American Chemical Society, June 1, 1904.

and washed once. The precipitate is washed back into the original casserole, 10 cc. concentrated hydrochloric acid added, and the solution diluted to 100 cc. It is once more made faintly ammoniacal, boiled a minute, then filtered and washed thoroughly, filtrate and washings being caught in the beaker containing the first filtrate. The precipitate is in a form which allows free and rapid filtration and washing. It contains the iron oxide and alumina, and the greater part, but by no means all of the silica present in the sample; generally about three-quarters or more of the total silica is precipitated here. It also contains, of course, small amounts of phosphates, titanic acid, etc., if present.

The filtrate, which has been caught in a beaker of about 20 ounces capacity, is slightly acidulated with hydrochloric acid, brought to a boil and 25 cc. of a saturated solution of ammonium oxalate added. When the clear solution again boils (it should be sufficiently acid to prevent precipitation of calcium oxalate) hot dilute ammonia is added with constant stirring until an excess equivalent to about 5 cc. of concentrated ammonia is introduced. Vigorous stirring and boiling is continued for five minutes, and the solution then set aside in a hot place for fifteen minutes longer. With the precautions noted carefully followed, complete precipitation of the lime will always take place in the time stated. The lime solution is kept acid until the time of precipitation to prevent the formation of calcium carbonate, which frequently happens while an ammoniacal solution of lime is being heated to the boiling-point. This precaution is very essential, as the method contemplates titration with potassium permanganate and it is necessary to have the lime precipitate entirely in the form of oxalate. Three washings by decantation and eight on the filter with hot water are sufficient to remove ammonium salts, etc.

The precipitate is then washed carefully with boiling water into a 16 ounce Erlenmeyer flask (care being taken to prevent the introduction of any pieces of filter-paper), dissolved by the addition of a small amount of hot dilute sulphuric acid, the paper also being washed once or twice with hot, very dilute acid, and the solution is immediately titrated with a potassium permanganate solution, which had previously been standardized by a standard cement, run in exactly the same manner, and in which the lime had been accurately determined by various methods.

This method of standardizing the permanganate solution is decidedly preferable to all others for the purpose intended, as by its use numerous errors, including that due to the solubility of calcium oxalate in hot water, which may, under certain circumstances, be a very considerable one, are entirely eliminated.

By this rapid method the percentage of lime in a cement can be arrived at in less than one-fifth the time ordinarily consumed in making this determination.

It might not be out of place to briefly note here some experiments, made by the writer several years ago, to determine the extent of the solubility of calcium oxalate under the conditions present in a cement or limestone analysis. Calcium oxalate precipitations, obtained from 0.5 gram and from 1 gram samples of cement by ordinary analysis, were filtered on 11 cm. papers, the size best used for this purpose. They were thoroughly washed (20 to 25 times) with boiling water to insure complete freedom from foreign salts. The washing of the pure oxalate precipitate was then continued with water at about 170° F., washings being combined, acidulated and titrated with a permanganate solution. Each washing on this size paper required approximately 25 cc. Blanks on the same amount of water and acid used, from the same flasks (the water being run through a filter-paper of the same quality and size), were also run, and their slight titration, 0.06 cc., subtracted.

Each combined five washings on the calcium oxalate from the 0.5 gram sample titrated 0.48 cc. to 0.54 cc., equivalent to 0.136 per cent. to 0.154 per cent. CaO, or 0.240 per cent. to 0.275 per cent. $CaCO_3$. The washings were continued indefinitely, each combination of five washings showing about the same titration. On the calcium oxalate precipitate from the 1 gram sample every combined five washings titrated the same, —0.48 cc. to 0.54 cc. The larger weight, however, reduced the percentage error one-half, the equivalents being 0.068 per cent. to 0.077 per cent. CaO, or 0.120 per cent. to 0.138 per cent. $CaCO_3$. This corresponds to 0.00123 to 0.00141 gram of anhydrous calcium oxalate, dissolved by approximately 100 cc. of hot water, the amount dissolved varying with the temperature. Richards, McCaffrey and Bisbee[1] found that 100 cc. of water at 95° C. dissolved 0.00140 gram, at 50° C. 0.0010 gram, and at 25° C. 0.00068 gram of the anhydrous oxalate.

[1] *Ztschr. anorg. Chem.*, **28**, 83 (1901).

The method described also practically eliminates the error due to solvent action of the solutions on the beakers, etc., used in the determination. A common practice in cement analysis is to catch the filtrate and washings from the calcium oxalate precipitate in a No. 6 beaker and boil or evaporate down to 100 to 150 cc. before precipitation of the magnesia. Whether this solution is kept ammoniacal during the evaporation, or, as more commonly practiced, rendered acid as soon as it is placed over the source of heat, a considerable solvent action takes place on the beaker during the operation. In numerous experiments made in actual determinations and also on blanks on reagents, water, etc., absolutely free from lime and silica this contamination was found at times to run as high as 0.0030 gram silica, equivalent on a 0.5 gram sample, to 0.60 per cent. silica, and 0.0024 gram, equivalent to 0.48 per cent. lime. While this silica possibly might not come down in the subsequent magnesia precipitate, the lime, if not previously removed, undoubtedly would, and would not be removed by a double precipitation of the ammonium magnesium phosphate. The resulting magnesia would consequently be high, contaminated with lime, obtained, not from cement itself, but from the glassware. If this lime were removed and added to that originally obtained in the regular course of analysis, a high lime determination would result. In the regular methods of analysis used a greater or less solvent action also occurs in the operations preceding the actual precipitation of calcium oxalate. In the rapid method described the solution is in contact with glass only a very short time before the precipitation of the lime, the solvent action is reduced to a minimum, and the possible error from this source is entirely obliterated by the fact that the potassium permanganate used in titration is standardized by a cement run under exactly the same conditions as the regular determinations.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

ACTION OF MUSTARD OILS AND ISOCYANATES ON HYDRAZO ACIDS.

BY J. R. BAILEY.

Received June 11, 1904.

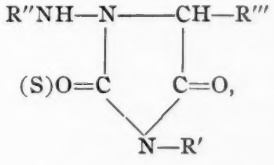
INTRODUCTION.

HYDRAZO compounds, as a rule, do not react readily with mustard oils,[1] although they react more readily with isocyanates.[2] In

[1] *Ber. d. chem. Ges.*, **25**, 3115.
[2] *Ibid.*, **23**, 490.

an investigation of semicarbazinopropionic acid ethyl ester,[1] the author, in conjunction with S. F. Acree, observed that this substance reacts with mustard oils, and further experiments have shown that α-hydrazo acids, in general, easily form compounds with both mustard oils and isocyanates; in fact, these reactions might well serve to characterize hydrazo acids. From the study of semicarbazinopropionic acid,[2] semicarbazinoisobutyric acid,[3] hydrazoisobutyric acid,[4] and phenylhydrazoisobutyric acid,[5] it appears probable that all α-hyrazo acids will show a similar behavior toward mustard oils and isocyanates.

The reaction product of a mustard oil on a hydrazo acid is not a simple addition product of one molecule on the other, but is this product minus one molecule of water. Although in the case of the isocyanates on hydrazo acids it is possible, sometimes, to isolate the primary reaction products, the latter also readily undergo ring condensation with the loss of water. The substances obtained are thiohydantoins and hydantoins, respectively, of the general formula

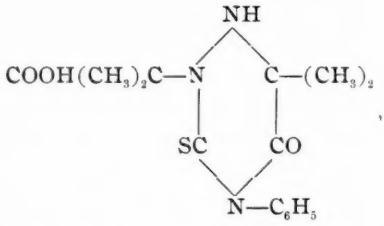


where R′, R″, R‴ represent, as usual, aliphatic or aromatic radicals. These formulas are proved conclusively by the chemical behavior of the substances in question.

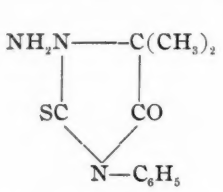
Hydrazoisobutyric acid, $COOH(CH_3)_2CNHNHC(CH_3)_2COOH$, gives with phenyl mustard oil a body which the analysis shows to be a condensation product of these two molecules minus a molecule of water. The substance so obtained is a monobasic acid, as is indicated by the titration with alkalies and the formation of esters. The possibility of the substance being a thiazole is excluded by the fact that it is readily desulphurized with mer-

[1] *Ann. Chem.* (Liebig), **303**, 83.
[2] *Loc. cit.*
[3] *Ann. Chem.* (Liebig), **283**, 33; *Am. Chem. J.*, **28**, 401.
[4] *Ann. Chem.* (Liebig), **290**, 25.
[5] *Ber. d. chem. Ges.*, **25**, 3323.

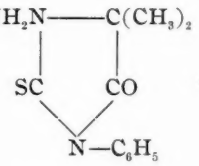
curic oxide, yielding a substance identical with the reaction product of phenylisocyanate on hydrazoisobutyric acid. The possibility of a triazine, constituted as follows,



is excluded by the behavior of the substance toward aqueous hydrochloric acid. Hydrochloric acid yields as a reaction product a substance that is undoubtedly 1-amino-5-dimethyl-3-phenyl-2-thiohydantoin,



In the formation of this substance an isobutyric acid radical is eliminated from the molecule, giving, as primary reaction products,

$(CH_3)_2C(OH)COOH$[1] and 

Such a reaction is analogous to the formation of hydrazine from hydrazinoisobutyric acid[2] and of hydrazine from 6-hydrazinopyridinecarboxylic acid-(3)[3] under the influence of aqueous hydrochloric acid. The formation of an aminothiohydantoin by the action of hydrochloric acid on the aminoisobutyric acid thiohydantoin, as described above, is further in accordance with the fol-

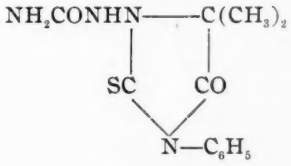
[1] No attempt was made to isolate this substance.
[2] *Ann. Chem.* (Liebig), **290**, 18.
[3] *Ber. d. chem. Ges.*, **36**, 1114.

lowing facts: The same substance is formed from hydrazinoisobutyric acid and phenyl mustard oil. The substance yields, with benzaldehyde, a yellow reaction product that is identical with a substance obtained from benzalhydrazinoisobutyric acid,

$$C_6H_5CH{=}NNHC(CH_3)_2COOH,^1$$

and phenyl mustard oil. It might seem anomalous that a substance, constituted like the aminothiohydantoin in question, does not possess basic properties, but Traube and Hoffa,[2] and later Busch and Holzmann[3] observed that aminothiohydantoins do not form salts with acids.

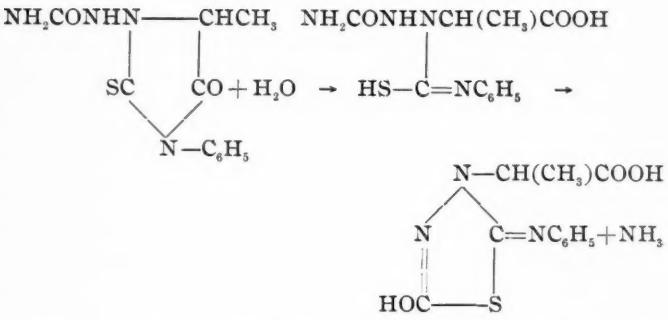
The substance obtained by the action of phenyl mustard oil on semicarbazinoisobutyric acid must also contain the thiohydantoin ring and be constituted as follows:



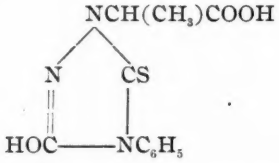
The above constitution is deduced from the fact that this compound wih hydrochloric acid yields 1-amino-5-dimethyl-3-phenyl-2-thiohydantoin, the constitution of which was established above. In this reacion the carbonamido radical of the ureidothiohydantoin is eliminated by interaction with a molecule of water. From the foregoing it appears probable that all α-hydrazo acids will react with mustard oils in a way similar to α-amino acids.[4]

5-Methyl-1-ureido-3-phenyl-2-thiohydantoin shows a peculiar behavior toward barium hydroxide in that it passes into 1,5-dihydro-3-oxy-5-phenylimido-4,1,2-thiodiazol-1-propionic acid, a reaction which may be interpreted by supposing the thiohydantoin ring hydrolyzed and the thiodiazole formed from this intermediary product by the elimination of a molecule of ammonia:

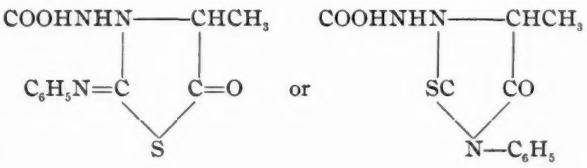
[1] *Ann. Chem.* (Liebig), **290**, 16.
[2] *Ber. d. chem. Ges.*, **31**, 322.
[3] *Ibid.*, **34**, 322.
[4] *Ibid.*, **17**, 420; **24**, 3278.



Another structural formula that would conform to the analytical data is a triazole,

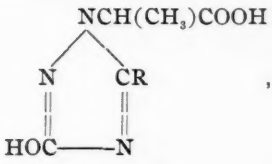


Such a substance is a cyclic amide and its formation in the presence of an alkali would not be expected, whereas thiazoles can be formed in alkaline solution.[1] Furthermore, the stability of the molecule toward mercuric oxide indicates that the sulphur is in a ring nucleus.



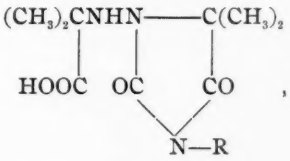
also represents a structural formula, in harmony with the analytical data, but improbable, in view of the instability of carbamic acids. This thiodiazole titrates as a dibasic acid and forms an amide, esters and a benzoyl derivative, properties which accord with the behavior of the somewhat similarly constituted triazoles of the general formula,

[1] *Ann. Chem.* (Liebig), **189**, 382.

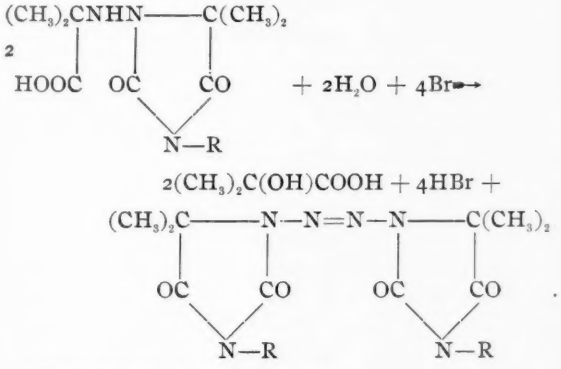


described by Bailey and Acree.[1]

The thiohydantoins of the general formula,



show an interesting behavior toward bromine water. Thiele and Hauser[2] studied the action of bromine water on hydrazoisobutyric acid derivatives and found that azo compounds are formed. As one of the imide hydrogens of the hydrazo groups is substituted in the substances under discussion, the formation of azo compounds is excluded here. It was found that the reaction products are tetrazones, a class of substances, the first representatives of which were prepared by E. Fischer.[3] The formation of these substances can be represented as follows:



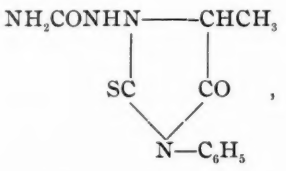
[1] *Ber. d. chem. Ges.*, **33**, 1520.
[2] *Ann. Chem.* (Liebig), **290**, 5.
[3] *Ibid.*, **190**, 166.

The amount of bromine used in this reaction was far in excess of that indicated by the equation, doubtless due to the bromination of the hydroxyisobutyric acid formed. Only one of these tetrazones, the one where R represents C_2H_5, was obtained in a condition pure enough for a satisfactory analysis. An attempt to determine the molecular weight, with chloroform as a solvent, of the tetrazone where R represents CH_3 gave results which indicate that a reaction of some kind is produced when these tetrazones are dissolved in chloroform. This fact offers a possible explanation of the slight discrepancies, in the case of two of the three tetrazones investigated, between the analytical data and the structural formulas ascribed to them. The study of these substances, as well as the study of the oxidation products of the corresponding thiohydantoins, will be continued.

Experimental Part.

Part I.—Action of Mustard Oils on Hydrazo Acids.

5-Methyl-1-ureido-3-phenyl-2-thiohydantoin,[1]



was first prepared as follows: Six grams of semicarbazinopropionic acid ethyl ester and 5 grams of phenyl mustard oil in alcoholic solution were heated to boiling one-half hour. At the end of this time 7.5 grams of the reaction product had crystallized out. The filtered solution, on evaporation to a small bulk and precipitation with ether, yielded a further small amount of the thiohydantoin. As the ester of the semicarbazino acid is somewhat difficult to obtain, the following method of preparing the hydantoin is to be preferred: One mole of freshly prepared semicarbazinopropionitrile[2] is allowed to stand two weeks with an aqueous solution of 0.5 mole of barium hydroxide in order to form the amide, and the barium is then removed as sulphate. The solution is now evaporated to

[1] The phenyl and allyl compounds were first prepared and analyzed conjointly with S. F. Acree.

[2] *Ann. Chem.* (Liebig), **303**, 79; *Am. Chem. J.*, **28**, 396.

a pasty mass and to this is added 1 mole of phenyl mustard oil, together with 10 cc. of 95 per cent. alcohol for each gram of nitrile employed. The alcoholic solution, after being boiled one hour, is evaporated to a small bulk and precipitated with ether. About 1 gram of the thiohydantoin is obtained for each gram of the nitrile employed. The thiohydantoin can be crystallized from water, alcohol or acetic ether. It crystallizes from methyl alcohol in aggregates of short, colorless prisms, as seen under the microscope, which decompose to a yellow liquid at 206°. An alcoholic solution of this substance does not produce a coloration with ferric chloride. On heating the thiohydantoin with hydrochloric acid the carbonamide radical is eliminated and an aminothiohydantoin formed. Treated with 0.5 mole of barium hydroxide at a temperature of 60°, the thiohydantoin ring is hydrolyzed and, by the elimination of ammonia, a thiodiazole formed. These reaction products are described further on.

Calculated for $C_{11}H_{12}O_2N_4S$: C, 50.00; H, 4.54; N, 21.21; S, 12.12. Found: C, 49.71; H, 4.72; N, 21.37; S, 12.04.

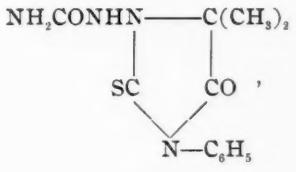
5-Methyl-1-ureido-3-allyl-2-thiohydantoin, prepared similarly to the corresponding phenyl compound by the action of allyl mustard oil on the ethyl ester of semicarbazinopropionic acid in alcoholic solution, melts at 167° to a clear liquid.

Calculated for $C_8H_{12}O_2N_4S$: C, 42.10; H, 5.26; N, 24.56; S, 14.03. Found: C, 41.87; H, 5.53; N, 24.65; S, 13.92.

5-Methyl-1-ureido-3-ethyl-2-thiohydantoin was prepared, similarly to the foregoing allyl compound, by the action of ethyl mustard oil on the semicarbazino ester. It crystallizes from alcohol in radiating bunches of short, microscopic prisms, which melt at 153°, apparently undecomposed, to a clear liquid.

Calculated for $C_7H_{12}O_2N_4S$: C, 38.89; H, 5.56; N, 25.93. Found: C, 38.86; H, 5.58; N, 26.21.

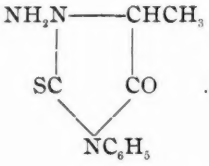
5-Dimethyl-1-ureido-3-phenyl-2-thiohydantoin,



was prepared in acetic ether solution from semicarbazinoisobutyric acid ethyl ester[1] and phenyl mustard oil by boiling the mixture one-half hour. Attempts to prepare the substance from other derivatives of this semicarbazino acid were without success. This thiohydantoin is readily soluble in alcohol, chloroform, acetic ether and benzene, difficultly soluble in water and as good as insoluble in ether and petroleum ether. It is best purified by precipitation from an alcoholic solution with ether. It decomposes at 191°, with gas evolution, to a clear liquid. Heated one hour with concentrated hydrochloric acid in a sealed tube at 140°, the substance passes into aminodimethylphenylthiohydantoin.

Calculated for $C_{12}H_{14}O_2N_4S$: C, 51.80; H, 5.04; N, 20.14; S, 11.51. Found: C, 51.67; H, 4.96; N, 20.19; S, 11.97.

1-Amino-5-methyl-3-phenyl-2-thiohydantoin,



—Seven grams of the corresponding ureidomethylphenylthiohydantoin, suspended in 100 cc. of concentrated hydrochloric acid were heated one hour in a sealed tube at 120°. Upon cooling the solution nothing immediately separated out, but, after letting off a slight pressure that was present and shaking the tube, the entire solution became filled with crystals. A little more than 2 grams of this new substance were thus obtained. On evaporating the filtrate to a small bulk and adding water a considerable amount of the original substance was recovered, unchanged. The compound crystallizes from water, or better, from alcohol, in long, slender, colorless, bayonet-shaped prisms, which melt at 150°, undecomposed. The substance is very soluble in chloroform, even in the cold, and difficultly soluble in alcohol and ether.

Calculated for $C_{10}H_{11}ON_3S$: C, 54.30; H, 4.98; N, 19.00. Found: C, 54.18; H, 5.20; N, 18.98.

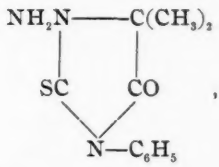
Treated with phenyl mustard oil in boiling alcoholic solution, aminomethylphenylthiohydantoin reacts to form a substituted sul-

[1] *Am. Chem. J.*, **28**, 402.

phourea, which separates from very dilute alcoholic solution in short, slender, microscopic prisms. This substance decomposes at 223° to a red liquid.

The analysis gave 15.48 per cent. N. Calculated for $C_{17}H_{16}ON_4S_2$, 15.73 per cent.

1-Amino-5-dimethyl-3-phenyl-2-thiohydantoin,



was obtained in several ways. It is formed similarly to the preceding compound, when dimethylureidophenylthiohydantoin is heated in concentrated hydrochloric acid under pressure at 140°. The compound crystallizes beautifully from alcohol in long needles, which melt undecomposed at 173°. It is readily soluble in cold chloroform, in benzene and in glacial acetic acid, more difficultly soluble in carbon disulphide and very difficultly soluble in water. The substance does not possess basic properties, but otherwise shows the characteristic reactions of a hydrazine. Two other methods of preparing this substance are described further on.

The analysis gave 17.75 per cent. N. Calculated for $C_{11}H_{13}ON_3S$, 17.87 per cent.

Reaction Product of Phenyl Mustard Oil on Aminodimethylphenylthiohydantoin.—The aminothiohydantoin was boiled with a slight excess of phenyl mustard oil in glacial acetic acid for one hour and the reaction product then precipitated by the addition of water. The same substance can be obtained by boiling hydrazinoisobutyric acid in acetic acid solution with an excess of mustard oil, when the acid reacts with 2 molecules of mustard oil. The behavior of hydrazino acids toward mustard oils can well serve to characterize the former substances.[1] For analysis the substance is best crystallized from glacial acetic acid, in which it is difficultly soluble. It is only slightly soluble in alcohol. It decomposes at about 233°.

The analysis gave 15.09 per cent. N. Calculated for $C_{18}H_{18}ON_4S_2$, 15.14 per cent.

[1] Compare *Ann. Chem.* (Liebig), **290**, 16.

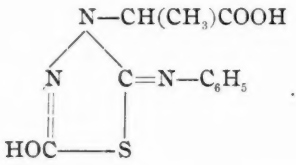
Reaction Product of Benzaldehyde on Aminodimethylphenylthiohydantoin.—The aminodimethylphenylthiohydantoin was heated in a test-tube with an excess of benzaldehyde until drops of water were formed on the side of the tube. The excess of aldehyde was then allowed to oxidize in the air and the benzoic acid thus formed was removed with ammonium hydroxide and the remaining trace of aldehyde with petroleum ether. The residue crystallized from alcohol as a light yellow substance, melting undecomposed at 135°. The hydrazone is more readily soluble in water than the corresponding aminothiohydantoin.

The analysis gave 12.93 per cent. N. Calculated for $C_{18}H_{17}ON_3S$, 13.00 per cent.

The foregoing substance was also prepared from benzalhydrazinoisobutyric acid, $C_6H_5CH{=}NNHC(CH_3)_2COOH$. The hydrazone in alcoholic solution was neutralized with potassium hydroxide and to this was added a little over one molecule of phenyl mustard oil. After boiling one-half hour, the solution, on cooling, solidified. The alcohol was next distilled off and the excess of mustard oil washed out with petroleum ether. The residue was then taken up with water and from the aqueous solution a substance was precipitated by the addition of hydrochloric acid. This proved identical with the reaction product of benzaldehyde on dimethylaminophenylthiohydantoin.

Calculated for $C_{18}H_{17}ON_3S$: C, 66.87; H, 5.26; N, 13.00. Found: C, 66.72; H, 5.22; N, 12.91.

1,5-Dihydro-3-oxy-5-phenylimido-4,1,2-thiodiazole-1-propionic acid,



—Ten grams of methylureidophenylthiohydantoin and 7 grams of barium hydroxide in 100 cc. of water were heated at 65° for four hours. The solution was then filtered and the thiodiazole precipitated by acidifying with hydrochloric acid. The yield of thiodiazole was 7.5 grams. The substance, after two crystallizations from water, melted at 220° with gas evolution to a brownish yellow

liquid. From water it crystallizes in radiating bunches of very fine needles. It is readily soluble in alcohol and chloroform, more difficultly soluble in ether and benzene. With ferric chloride the thiodiazole gives characteristic color reactions; in absolute alcohol it gives, with an alcoholic solution of ferric chloride, a greenish blue color, which, on the addition of a few drops of water, becomes an intense blue. This blue color in less than a minute's time passes into an amethyst color and, on further dilution, the solution, after standing some time, assumes a faint green color. The thiodiazole titrates as a dibasic acid, requiring only a little less than the calculated two molecules of sodium hydroxide for neutralization. With mercuric chloride in alcoholic solution it gives a very difficultly soluble double salt, which was not further investigated. An attempt to split off aniline, by heating the thiodiazole with concentrated hydrochloric acid, was not successful. In contrast to the thiohydantoins, discussed in this paper, an ammoniacal solution of the thiodiazole can be boiled with mercuric oxide without forming mercuric sulphide.

Calculated for $C_{11}H_{11}O_3N_3S$: C, 49.81; H, 4.15; N, 15.85; S, 12.08. Found: C, 49.61; H, 3.90; N, 15.89; S, 12.20.

Titration of the thiodiazole with N/10 NaOH:

0.2156 gram substance required 15.75 cc. N/10 NaOH; calculated, if dibasic, 16.26 cc.

0.2180 gram substance required 16.05 cc. N/10 NaOH; calculated, if dibasic, 16.44 cc.

For the titration the acid was dissolved in alcohol and phenolphthalein used as an indicator.

1,5-Dihydro-3-oxy-5-phenylimido-4,1,2-thiodiazole-1-propionic Acid Ethyl Ester.—The ester was prepared by boiling 3 grams of the acid with 50 cc. of 4 per cent. alcoholic hydrochloric acid one hour. The solution was then evaporated to dryness and taken up with water. The ester is a monobasic acid, readily soluble in alkalies and ammonia, and difficultly soluble in water. It is more soluble in benzene, and more difficultly soluble in ether and alcohol, than the acid. For the analysis the substance was purified by crystallization from benzene and finally from dilute alcohol. It melts undecomposed at 171°. The color reactions produced in an alcoholic solution of the ester with ferric chlorides are very similar to those observed in the case of the corresponding acid.

Calculated for $C_{13}H_{15}O_3N_3S$: C, 53.24; H, 5.12. Found: C, 53.48; H, 5.24.

In the titration of the ester in alcoholic solution with N/10 NaOH with phenolphthalein as indicator, 0.5920 gram substance required 20.3 cc.; calculated, 20.2 cc.

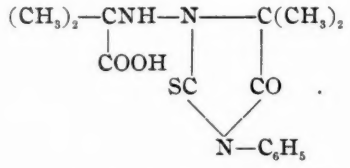
Benzoyl Derivative of the Ester.—This substance may be prepared from the sodium salt of the ester by boiling this with 1 molecule of benzoyl chloride in benzene solution. It is readily soluble in alcohol and benzene and best purified by crystallization from the latter. It crystallizes in broad, thin plates, which melt undecomposed at 110°. Unlike the ester and acid, the benzoyl derivative of the ester gives no color reaction with ferric chloride.

The analysis gave 10.63 per cent. N. Calculated for $C_{20}H_{19}O_4N_3S$, 10.58 per cent.

1,5-Dihydro-3-oxy-5-phenylimido-4,1,2-thiodiazole-1-propionic Acid Amide.—Three grams of the ethyl ester were dissolved in 50 cc. of alcoholic ammonia and the solution allowed to stand one month. On evaporation of the alcohol the amide remained as an ammonium salt. This was dissolved in water and the amide precipitated with hydrochloric acid. For purification the substance was twice crystallized from alcohol. It melts at 228° with gas evolution to a brownish yellow liquid.

The analysis gave 21.46 per cent. N. Calculated for $C_{11}H_{12}O_2N_4S$, 21.21 per cent.

5-Dimethyl-3-phenyl-1-isobutyric-acid-amino-2-thiohydantoin,[1]



—After numerous experiments the following method was found to give the best results in the preparation of the above thiohydantoin: Twenty-five grams of hydrazoisobutyric acid and 20 grams of phenyl mustard oil in 100 cc. of glacial acetic acid as solvent are heated one hour to boiling. The acetic acid is now removed for the greater part by distillation *in vacuo* and the hydantoin precip-

[1] The preparation of the phenyl and allyl derivatives, as well as the esters described under the phenyl compound, was carried out conjointly with P. T. Miller.

itated by the addition of water. This method gave a yield of about 92 per cent. of the theoretical, although the hydrazo acid was not quite pure. The thiohydantoin thus obtained is readily soluble in ether, alcohol, chloroform and benzene, less readily soluble in carbon disulphide and rather difficultly soluble in water. The thiohydantoin differs from hydrazoisobutyric acid in that it does not possess basic properties and is, therefore, not readily soluble in acids. For analysis the substance was crystallized from benzene and ether. It melts at 153°. The presence of a carboxyl group is shown by the formation of esters and the presence of an imide group by the formation of a nitroso compound. The thiohydantoins, obtained by the action of mustard oils on hydrazoisobutyric acid, are readily desulphurized with mercuric oxide. The products thus obtained are described further on. Hydrochloric acid eliminates the isobutyric acid radical, yielding aminodimethylphenylthiohydantoin, the reaction product of hydrochloric acid on ureidodimethylphenylthiohydantoin and of phenyl mustard oil on hydrazinoisobutyric acid.

Calculated for $C_{15}H_{19}O_3N_3S$: C, 56.07; H, 5.92; N, 13.09; S, 9.97. Found: C, 56.46; H, 6.13; N, 13.09; S, 9.97.

Titration of the Dimethylphenylisobutyric-acid-aminothiohydantoin with N/10 NaOH:

0.1829 gram substance required 5.7 cc. N/10 NaOH; calculated, if monobasic, 5.7 cc. N/10 NaOH.

Action of Hydrochloric Acid on Dimethylphenylisobutyric-acid-aminothiohydantoin.—Five grams of the thiohydantoin were heated at 140°-160° with 60 cc. concentrated hydrochloric acid in a sealed tube for one hour. On cooling the tube it was found that complete solution had been effected. However, after letting off the pressure in the tube 2.4 grams of a new substance quickly separated out. The substance was prepared for analysis by crystallization from methyl alcohol and benzene.

Calculated for $C_{11}H_{13}ON_3S$: C, 56.17; H, 5.53; N, 17.87; S, 13.62. Found: C, 56.17; H, 5.77; N, 17.86; S, 13.75.

This substance has the same melting-point, 173°, as the reaction product already described of hydrochloric acid on 5-dimethyl-1-ureido-3-phenyl-2-thiohydantoin, and the two preparations, when mixed in equal amounts and crystallized from alcohol, form crystals, which possess a constant melting-point of 173°. The two preparations are, therefore, undoubtedly identical. The same sub-

stance may also be prepared from hydrazinoisobutyric acid, $NH_2NHC(CH_3)_2COOH$, and phenyl mustard oil, when they are allowed to react in molecular proportion. The hydrazine is dissolved in a little water and to this is added the mustard oil in alcohol and the mixture is then heated about twenty minutes to boiling. The aminothiohydantoin can be separated from a little of the reaction product of 2 molecules of mustard oil on the hydrazinoisobutyric acid by dissolving out the former with chloroform. A third body, readily soluble in alcohol, is formed in small amount in this reaction, but this was not investigated.

Nitroso Derivative of 5-Dimethyl-3-phenyl-1-isobutyric-acid-amino-2-thiohydantoin.—When double the calculated amount of sodium nitrite in concentrated aqueous solution is slowly added to a cold glacial acetic acid solution of the thiohydantoin a nitroso body is formed and may be precipitated by pouring the acetic acid solution into a large excess of water. The substance, purified by crystallization from a benzene-ligroin mixture, melted with gas evolution to a brown liquid at 166°. It shows the Liebermann reaction.

The analysis gave 16.06 per cent. N. Calculated for $C_{15}H_{18}O_4N_4S$, 16 per cent.

Ethyl Ester of 5-Dimethyl-3-phenyl-1-isobutyric-acid-amino-2-thiohydantoin.—To effect esterification, 3 grams of the acid were put into 110 cc. of 4 per cent. alcoholic hydrochloric acid and the solution boiled one hour. The alcohol was then distilled off, the residue taken up with water, and the ester precipitated with sodium bicarbonate. Purified by crystallization from dilute methyl alcohol, it melted at 84°. By evaporation of the benzene solution of the ester, it can be obtained in large four-sided prisms.

The analysis gave 12.11 per cent. N. Calculated for $C_{17}H_{23}O_3N_3S$, 12.04 per cent.

Methyl Ester.—This ester, prepared similarly to the ethyl ester, is much more difficultly soluble in alcohol. It melts undecomposed at 142°.

Calculated for $C_{16}H_{21}O_3N_3S$: C, 57.31; H, 6.27; N, 12.54; S, 9.55. Found: C, 57.47; H, 6.37; N, 12.66; S, 9.75.

5-Dimethyl-3-allyl-1-isobutyric-acid-amino-2-thiohydantoin can be obtained in almost theoretical yield by the method employed in the preparation of the corresponding phenyl compound. The sub-

stance, purified by recrystallization from benzene, melts undecomposed at 121°. It can be crystallized from water in very pointed diamond-shaped plates.

Calculated for $C_{12}H_{19}O_3N_3S$: C, 50.53; H, 6.67; N, 14.74. Found: C, 50.62; H, 6.82; N, 14.92.

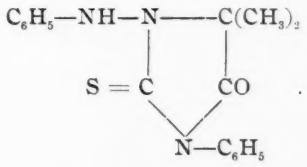
5-Dimethyl-3-ethyl-1-isobutyric-acid-amino-2-thiohydantoin, purified by crystallization from dilute alcohol and then from benzene, melted undecomposed at 110°.

Calculated for $C_{11}H_{19}O_3N_3S$: C, 48.35; H, 6.96; N, 15.38; S, 11.72. Found: C, 48.41; H, 6.64; N, 15.47; S, 11.63.

5-Dimethyl-3-methyl-1-isobutyric-acid-amino-2-thiohydantoin, purified similarly to the corresponding ethyl compound, melts apparently undecomposed to a clear liquid at 129°.

The analysis gave 16.20 per cent. N. Calculated for $C_{10}H_{17}O_3N_3S$, 16.22 per cent.

5-Dimethyl-3-phenyl-1-phenylamino-2-thiohydantoin,[1]



—This substance, prepared in glacial acetic acid solution by allowing phenyl mustard oil and phenylhydrazoisobutyric acid to react in molecular proportion, was purified by crystallization from alcohol, acetic ether and finally benzene. It melts, apparently undecomposed, at 206°. This thiohydantoin is readily soluble in common organic solvents, petroleum ether excepted, and almost insoluble in water.

Calculated for $C_{17}H_{17}ON_3S$: C, 65.59; H, 5.47; N, 13.50; S, 10.29. Found: C, 65.64; H, 5.73; N, 13.53; S, 10.18.

5-Dimethyl-3-ethyl-1-phenylamino-2-thiohydantoin, prepared similarly to the foregoing compound from ethyl mustard oil and phenylhydrazoisobutyric acid, and purified by crystallization from dilute alcohol and petroleum ether, melts at 85°.

The analysis gave 15.94 per cent. N. Calculated for $C_{13}H_{17}ON_3S$, 15.97 per cent.

[1] The investigation of the behavior of mustard oils toward phenylhydrazoisobutyric acid was carried out conjointly with Ernest Anderson.

PART II. ACTION OF PHENYLISOCYANATE ON HYDRAZO ACIDS. DESULPHURIZATION OF THIOHYDANTOINS.

α-Ureido-α,β-diphenylurea,

$$C_6H_5NHCON(C_6H_5)NHCONH_2.$$[1]

—To prepare this substance phenylsemicarbazide,

$$NH_2CONHNHC_6H_5,$$

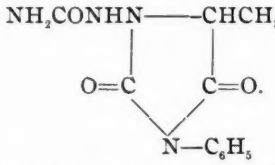
and an excess of phenylisocyanate are allowed to react for several hours in boiling benzene. The insoluble reaction product is then filtered off and purified by crystallization from alcohol, in which it is difficultly soluble. It melts with gas evolution to a clear liquid at 210°. Unlike phenylisocyanate, phenyl mustard oil does not react with phenylsemicarbazide at the boiling temperature of benzene.

Calculated for $C_{14}H_{14}O_2N_4$: C, 62.22; H, 5.19; N. 20.74. Found: C, 62.24; H, 5.29; N, 21.00.

Action of Phenylisocyanate on Semicarbazinopropionic Acid Ethyl Ester.—Two grams of $NH_2CONHNHCH(CH_3)COOC_2H_5$ were suspended in 50 cc. of benzene and then 1.5 grams of phenylisocyanate added. Reaction took place immediately with considerable elevation of temperature and the ester quickly dissolved. To complete the reaction the solution was boiled one hour. The benzene was next distilled off and the residue crystallized from alcohol and acetic ether. The new substance melts at 163°. The analysis shows this substance to be a simple addition product of the isocyanate on the semicarbazino ester, *i. e.*, *α*-phenylcarbonamidesemicarbazinopropionic acid ethyl ester, $NH_2CONHN(CONHC_6H_5)CH(CH_3)COOC_2H_5$.

Calculated for $C_{13}H_{18}O_4N_4$: C, 53.06; H, 6.12; N, 19.05. Found: C, 53.00; H, 6.24; N, 19.29.

The above substance, when boiled in water solution, readily splits off alcohol, giving 5-methyl-1-ureido-3-phenylhydantoin,

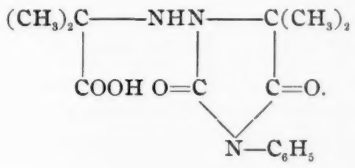


[1] The investigation of the reaction products of phenylisocyanate on phenylsemicarbazide and on semicarbazinopropionic acid ethyl ester was carried out conjointly with P. T. Miller.

This latter substance crystallizes from acetic ether in long, very slender needles, which decompose at about 219°.

Calculated for $C_{11}H_{12}O_3N_4$: C, 53.23; H, 4.84. Found: C, 53.24; H, 4.97.

5-Dimethyl-3-phenyl-1-isobutyric-acid-aminohydantoin,



—This substance was obtained by desulphurizing the corresponding 2-thiohydantoin, already described, and also by allowing phenylisocyanate to react on hydrazoisobutyric acid in glacial acetic acid solution. One hundred cc. of glacial acetic acid, in which were dissolved 10 grams of phenylisocyanate and 16 grams of hydrazoisobutyric acid, were boiled one hour, the acetic acid was then boiled off *in vacuo,* and the residue crystallized from alcohol. In this way 12.5 grams of the hydantoin were obtained. The alcohol, on evaporation, yielded a large amount of s-diphenylurea and 2 grams of the hydantoin. The latter was dissolved with sodium bicarbonate and then regained by precipitation with hydrochloric acid. The substance is difficultly soluble in benzene, almost insoluble in ether and water, and readily soluble in hot alcohol. From the latter it crystallizes in characteristic prisms with wedge-shaped end faces. It melts at 205° to a light brown liquid. Like the corresponding 2-thiohydantoin, it titrates as a monobasic acid.

Calculated for $C_{15}H_{10}O_4N_2$: C, 59.02; H, 6.23; N, 13.77. Found: C, 58.93; H, 6.24; N, 13.83.

0.4128 gram substance required 13.48 cc. N/10 NaOH; calculated, if monobasic, 13.53 cc. N/10 NaOH.

Ethyl Ester of 5-Dimethyl-3-phenyl-1-isobutyric-acid-aminohydantoin.—This ester was prepared similarly to the ethyl ester of the corresponding 2-thiohydantoin. It is readily soluble in alcohol, benzene and ether, and difficultly soluble in petroleum ether and water. For the analysis it was twice crystallized from ether, from which it separates in large hexagonal prisms. The substance melts undecomposed at 98°.

Calculated for $C_{17}H_{23}O_4N_3$: C, 61.26; H, 6.91; N, 12.61. Found: C, 61.14; H, 6.89; N, 12.66.

Action of Mercuric Oxide on 5-Dimethyl-3-phenyl-1-isobutyric-acid-amino-2-thiohydantoin.—Three grams of the above thiohydantoin were converted into the sodium salt by dissolving it in the calculated amount of N/10 NaOH, and this solution, diluted to 150 cc., was heated for one hour in a boiling water-bath with a large excess of mercuric oxide. The solution was then filtered and a substance precipitated by acidifying with hydrochloric acid that proved identical in every respect with the reaction product, already described, of phenyl isocyanate on hydrazoisobutyric acid.

Calculate for $C_{15}H_{19}O_4N_3$: C, 59.02; H, 6.23; N, 13.77. Found: C, 58.88; H, 6.25; N, 13.81.

3-Methyl-5-dimethyl-1-isobutyric-acid-aminohydantoin.—After several experiments, the following method of preparing this hydantoin was adopted as giving the best yield: The corresponding 2-thiohydantoin is dissolved in a slight excess of ammonium hydroxide and then an excess of mercuric oxide added. Reaction takes place in the cold, with an elevation of temperature in the solution, and the mercuric oxide is quickly blackened. The solution is allowed to stand fifteen hours with occasional shaking. At the end of this time the hydantoin is isolated in the manner described under the 3-phenyl compound. This method gave a yield of 7.7 grams of hydantoin from 12 grams of the thiohydantoin. It is not at all necessary to purify the thiohydantoin, as even a very impure substance yields an almost pure product. This hydantoin is readily soluble in alcohol, ether and benzene, and crystallizes beautifully from water in slender prisms, melting at 169°.

Calculated for $C_{10}H_{17}O_4N_3$: C, 49.38; H, 7.00; N, 17.28. Found: C, 49.26; H, 7.11; N, 17.24.

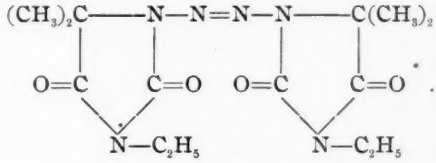
3-Ethyl-5-dimethyl-1-isobutyric-acid-aminohydantoin was prepared similarly to the foregoing substance by desulphurizing the corresponding 2-thiohydantoin. It has about the same solubility as the 3-methyl compound and crystallizes from water in long, slender needles, which melt at 140°.

Calculated for $C_{11}H_{19}O_4N_3$: C, 51.36; H, 7.39. Found: C, 51.29; H, 7.43.

5-Dimethyl-3-allyl-1-isobutyric-acid-aminohydantoin, obtained by desulphurizing the corresponding 2-thiohydantoin, was purified by crystallization from water and ether. It crystallizes in thin, prismatic plates, which melt at 114°.

Calculated for $C_{12}H_{19}O_4N_5$: C, 53.53; H, 7.06; N, 15.61. Found: C, 53.23; H, 7.09; N, 15.77.

1-Azo-5-dimethyl-3 ethylhydantoin,[1]



—The aminoisobutyric-acid-hydantoins, as well as the corresponding thiohydantoins, behave as reducing agents toward bromine water or potassium permanganate. Although these oxidation products have not been thoroughly investigated, the analyses thus far made indicate that they are tetrazones. The method of preparing these substances is to suspend the hydantoin in water, or better, to dissolve it in alcohol, and then add bromine water until the bromine produces a faint, permanent yellow color. A large amount of the bromine is probably used in brominating the oxyisobutyric acid split off in this reaction. Three grams of dimethylethylisobutyric-acid-aminohydantoin required 510 cc. $^9/_{100}$ N bromine water. In this experiment 1.9 grams of the tetrazone were obtained. The tetrazones here described are very difficultly soluble in almost all solvents thus far tried, except chloroform and glacial acetic acid. They can be obtained snow-white by precipitation with petroleum ether from a chloroform solution, but this method of crystallization does not seem to effect complete purification. For analysis the azodimethylethylhydantoin was twice crystallized from alcohol and thus obtained as a crystalline white substance, which melts with gas evolution at 234°.

Calculated for $C_{14}H_{22}O_4N_8$: C, 49.70; H, 6.51; N, 24.85. Found: C, 49.64; H, 6.59; N, 24.88.

1-Azo-3-methyl-5-dimethylhydantoin was prepared similarly to the preceding 3-ethyl compound. It was purified by precipitation

[1] This nomenclature is not strictly in accordance with the recognized use of the term "azo," which is employed to designate the group N=N doubly joined to carbon, but this extended application of the term here removes the difficulty that would arise were it attempted to embody the term "tetrazone" in the name of these substances.

from a chloroform solution with petroleum ether. The product thus obtained decomposed at about 278°. The nitrogen determinations, which were made on different preparations, were between 0.5 per cent. and 1 per cent. below the theoretical in each case.

Calculated for $C_{12}H_{18}O_4N_6$: C, 46.45; H, 5.85; N, 27.10. Found: C, 46.22; H, 5.90; N, 26.36, 26.16, 26.60.

1-Azo-5-dimethyl-3-phenylhydantoin was prepared and purified similarly to the foregoing tetrazone. It decomposes to a brown liquid at 270° with gas evolution. The product analyzed had the external appearance of purity, but the analytical data do not conform closely to the formula given this substance.

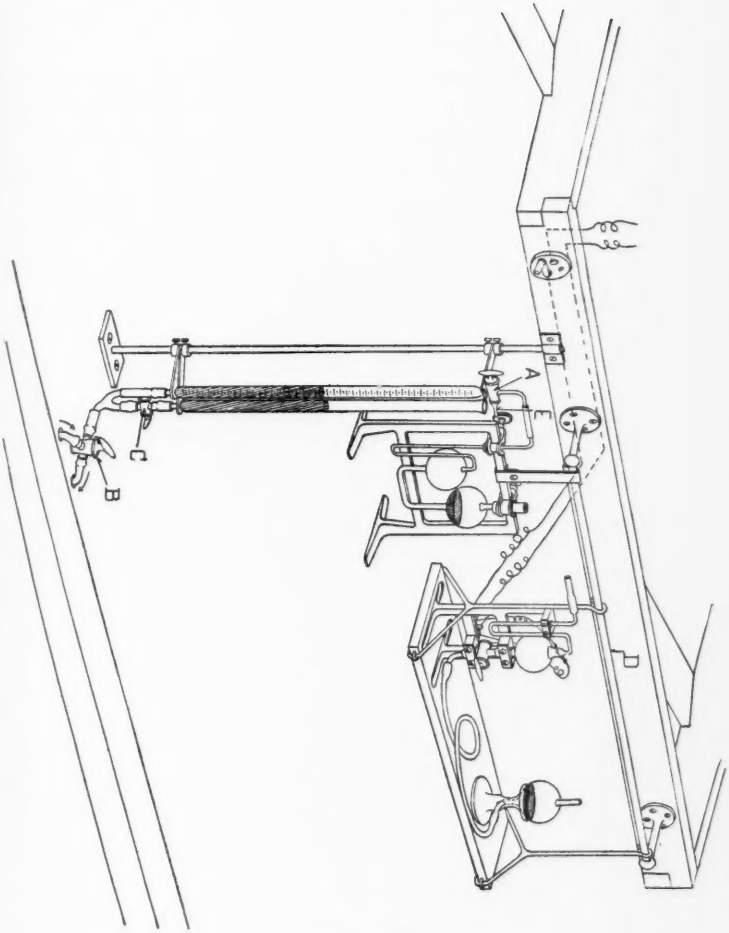
Calculated for $C_{22}H_{22}O_4N_6$: C, 60.83; H, 5.07; N, 19.35. Found: C, 61.85; H, 5.26; N, 18.71, 18.90.

NOTES.

Stationary Hempel Apparatus.—The apparatus shown in the accompanying sketch was devised by Mr. W. J. Knox, of Pittsburg, and has been in constant use for a number of years with no radical modifications.

To a horizontal frame, near to and parallel to the edge of the working-bench, is attached a horizontal rod, D, about 5/8 inch in diameter, on which the pipettes may be suspended from appropriate hooks attached to the frame of the pipette, while to a vertical rod, secured to frame and bench, are fastened the burette and leveling tube in such a manner as to permit free lateral motion. The prolong of the burette is bent at right angles to the burette and parallel to the graduations. The capillary tubes of the pipettes are also bent to 90°, so that only a single rubber connection is necessary to attach the pipette to the burette. At the top of the burette is a 3-way cock, A, the second outlet, E, being the stem of the cock. At the bottom of the leveling tube is a cock, C. Burette and leveling tube are connected by a Y-tube to one branch of a 3-way cock, B, the other branches of which are connected, respectively, to an overhead reservoir and drain.

The *modus operandi* is as follows: With C closed, open A to burette and fill burette with water by opening B to supply. Close A and attach sample bottle to prolong of burette. Pass enough


A
B
C

gas through E to insure complete elimination of air. Open A to burette and draw in sample by opening B to drain. To obtain the volume at atmospheric pressure: With A closed, open C and, by admitting or withdrawing water, by means of B, the level of burette and leveling tube is easily obtained.

With A still closed, attach the appropriate pipette to the prolong of burette; open A to burette and force gas into pipette by filling burette with water by means of B. When absorption is complete, return gas to burette by opening B to drain; then level, as described above. If it is desired to shake the pipette, a swinging motion may be given to it without disconnecting from the burette. The rod D is long enough so that the hanging shelf, on which the explosion pipette and mercury reservoir are placed, may be thrown back out of the way when not in use. The ordinary absorbents are used.

H. C. BABBITT.

EAST PITTSBURG GAS WORKS,
EAST PITTSBURG, PA.

Note on the Standardization of Iodine Solutions.—During the course of some extensive investigations upon sodium thiosulphate, the thought suggested itself that very possibly the anhydrous salt might be readily prepared in a state of sufficient purity to serve as a reagent for the standardization of the iodine solutions used in the work. This has been found to be the case, and a very simple and practical, as well as exact, method has been devised for accomplishing this.

The anhydrous thiosulphate is best prepared by recrystallizing the chemically pure salt of commerce from warm solutions (saturated at from 30° to 35° C.) by cooling and constant stirring. The salt thus obtained is of about the grain of granulated sugar, and is to be dried on filter-paper at room temperature. It is then dehydrated over sulphuric acid until it has fallen to a powder, and a portion in a test-tube shows no sign of fusion when heated to 50°. The final dehydration is carried on in an air-bath at about 80°, with repeated stirring of the powder. For relatively small quantities two hours' heating will usually be sufficient. The salt is then to be placed in a tight-stoppered weighing-bottle, from which samples are taken as desired.

Following are some results obtained by the use of this salt. The method was simply to take a weighed sample, dissolve in water and titrate with the iodine solution to the appearance of the

blue color with starch solution. The figures are grams of thiosulphate, equivalent to 1 cc. of iodine solution.

Weight of sample.	Volume of iodine solution. cc.	Standard of solution.
0.8833	27.45	0.03228
0.7288	22.57	0.03227
0.9319	28.90	0.03224
0.6807	21.07	0.03229

The standard of the same iodine solution, as determined by the direct method with a weighed quantity of iodine, was 0.03228.

Three days later the following determinations were made with the same substance in order to see if there was any deterioration of the anhydrous salt within that time, due, perhaps, to absorption of moisture or other cause.

Weight of sample.	Volume of iodine solution. cc.	Standard of solution.
0.9404	29.30	0.03210
0.8338	25.92	0.03217
0.6100	18.92	0.03224
0.8518	26.47	0.03218

Two determinations by the direct method, made at the same time, gave 0.03217 and 0.03221.

Except for the first determination, the agreement is all that could be desired. There is more than likely a small experimental error in the first determination. S. W. YOUNG.

STANFORD UNIVERSITY,
May 19, 1904.

Note on the Effect of Old Filter-paper on Iodate-free Potassium Iodide.—In the course of some experiments with potassium iodide it developed that a dilute solution (1 in 10) of iodate-free salt, after filtering through the ordinary filter-paper of the laboratory and acidification with a few drops of dilute sulphuric acid after the manner of the United States Pharmacopœia test for iodate,[1] oftentimes showed a distinct brownish coloration after

[1] The Pharmacopœia of 1890 recommends the use of starch paste to render the liberation of iodine evident by the formation of the characteristic starch-iodine blue. We find that the yellow coloration of the free iodine is as delicate and as easily seen in a colorless clear solution as the starch reaction. Hence we omitted the starch paste. We worked with 1 gram of potassium iodide in 10 cc. of water instead of 1 gram in 20 cc. as directed in the Pharmacopœia. In all these tests it is necessary to run a blank on the iodide solution along with the test, since, as is well known, the acidified potassium iodide solution becomes brownish from the oxidation of the hydriodic acid by the oxygen of the air. If the time of standing be short, say three minutes, the blank solutions will be practically water-white, whereas the solutions treated with old filter-paper will be distinctly yellowish. The coloration corresponds, of course, to a very small weight of iodine: For 20 cc. of the solution, it required only two or three drops of N/100 thiosulphate solution to cause a complete bleaching.

several minutes standing, due, of course, to the liberation of traces of iodine. With some filters and with washed glass wool the effect was absent and the acidified, clear solution remained water-white for a few minutes. The iodate-free potassium iodide was prepared by acting upon a slightly alkaline, dilute solution of the salt in nitrite-free water with magnesium powder and shaking. This solution, after being filtered to remove the magnesium, gave the above slight test for iodate, indicating the paper as the cause of the trouble.

Samples of paper from other rooms in the same laboratory were then tested in the above manner, and also with indigo solution, with the result that out of sixteen samples of various papers all but two colored the potassium iodide solution and these two did not bleach the indigo. The indigo reaction was tried on four of the samples which colored the iodide and each time the blue solution bleached slightly, but distinctly. The papers tested included the ordinary sheet filter-paper, factory filters (gray and white), Schleicher & Schüll's quantitative (washed), and several grades of Dreverhoff's best. All these papers had been kept in different laboratory rooms and in different drawers for times varying from several months to a year.

It is quite well-known that filter-paper absorbs or occludes gases somewhat in the manner of charcoal when exposed, and recently H. R. Procter[1] has pointed out that filters, originally free from acidity or alkalinity, easily absorb acids or ammonia from the laboratory air in sufficient quantity to disturb titrations for hardness in water analysis and, accordingly, he recommends thorough washing and rejection of part of the first filtrates. Mansier,[2] working with solutions, found that filter-paper, like bone-coal, has the power of fixing certain substances in the fibers so that washing will not remove them. For example, he found that a 15 cm. filter, previously thoroughly extracted with dilute hydrochloric acid followed by distilled water, lowered the strength of a normal solution of sodium hydroxide by about a twentieth of its original value. The paper was immersed in the solution, which, presumably, was then decanted and titrated.

L. W. Andrews[3] has detected nitrites in filter-paper which has stood for some time exposed to laboratory air. With these facts

[1] *J. Soc. Chem. Ind.*, January 15, 1904.

[2] Mansier: *J. Pharm. Chim.* [6], **16**, 6-116 (1902); abstract in *Centrbl.*, **2**, 768 (1902).

[3] Private communication: Dr. Andrews further states that some of the papers containing no nitrites still liberated iodine from potassium iodide. The cause of this is not known to us.

in mind we tested old papers again for nitrous acid by the characteristic Griess reaction along with the various grades of *fresh papers,* obtained directly from Eimer & Amend. The procedure was as follows: Six sheets (7 cm.) of the fresh paper from different parts of the pack were torn to pieces and treated for fifteen minutes with 60 cc. of nitrite-free water, and this solution was poured into Nessler tubes, about 2 cc. of the sulphanilic acid solution added, followed by about 2 cc. of the α-naphthylamine solution. The amounts of nitrogen present as nitrites were estimated colorimetrically by comparing the colors obtained from the filter-paper solutions with a scale of colors produced by adding definite amounts of a determinate sodium nitrite solution, as is usual in water analysis.[1] Quantities of peroxide of hydrogen and of sodium hypobromite, greatly in excess of the equivalent of the maximum amount of nitrite, measured in the filter-paper, gave no characteristic coloration when treated with the Griess reagents. Measured in this way, the six sheets (7 cm.), representing 3 to 4 grams of the various fresh papers, including Eimer & Amend's best white, The Baker & Adamson Chemical Co.'s hydrofluoric and hydrochloric washed, Munktell's Swedish paper and Schleicher & Schüll's, gave only *very slight tests* for nitrites, corresponding roughly to from 0.0001 mg. to 0.0005 mg. of nitrogen, according to the different makes used. On the other hand, the old paper which had been kept in the laboratory for some time invariably gave a *strong reaction.* Thus two sheets (7 cm.) of Eimer & Amend's best white from a drawer in the laboratory showed over 0.0020 mg. of nitrogen, corresponding to more than 0.0060 mg. of nitrogen for six papers, and two sheets of Schleicher & Schüll's (7 cm., No. 589) from the same drawer showed over 0.0008 mg., corresponding to more than 0.0024 mg. for six papers. We found, furthermore, that 2 grams of a large Prat-Dumas filter, which had been kept in an office room off from the laboratory, showed 0.0001 mg. of nitrogen, but the same amount of a similar filter, which had remained in the laboratory for some time, showed 0.0020 mg. nitrogen. As would be expected, the fresh papers showed no coloration with potassium iodide solutions and of the Prat-Dumas paper above mentioned, the sheets stored in the laboratory gave a strong reaction, whereas that stored in the office desk showed none.

[1] Solutions according to Richards and Woodman: "Air, Water, and Food." α-naphthylamine 8 grams, concentrated hydrochloric acid 8 cc., water 992 cc. Sulphanilic acid 8 grams in 1 liter of water.

The above experiments confirm the results of Andrews and show that just as the absorption of acid vapors by filter-paper exposed to laboratory air may render the paper unfit for delicate titrations, as, for example, the determination of the hardness of water, so also the absorption of nitrous vapors may take place to such an extent as to oxidize solutions of iodate-free potassium iodide when filtered through such paper. With the paper used in these experiments the oxidation, although representing very small amounts of free iodine, was readily detectable by the appearance of a yellowish coloration when such a solution is acidified.

E. MALLINCKRODT, JR., AND W. N. STULL.

LABORATORY OF THE MALLINCKRODT CHEMICAL WORKS,
ST. LOUIS, MO.

NEW BOOKS.

A COMPENDIUM OF CHEMISTRY, INCLUDING GENERAL, INORGANIC, AND ORGANIC CHEMISTRY. BY DR. CARL ARNOLD. Translation by JOHN A. MANDEL, Sc.D. New York : John Wiley and Sons. Price, $3.50.

Dr. Arnold is a professor of chemistry at Hannover, and the German original has held its place for twenty years and through eleven editions. It is obvious that such a book must possess qualities which will lead chemists in this country to welcome a translation. This contains 600 closely packed pages. 100 are devoted to general chemistry, 100 to the non-metallic elements, 100 to the metals, and 300 to organic chemistry. No space is given up to illustrations, none to history, none even to names of great chemists and discoverers, except as apparatus or laws may be called after them. Type of two sizes is employed, statements are usually brief, and the amount of information here compressed is surprising. It has an index containing not less than 5,550 entries. Together with this wealth of content the book has other excellencies which will commend it to those to whose wants it is adapted.

The original is called a *Repetitorium;* it may well take the place of those notes of a lecture course which few junior students can make without sacrificing the most profitable kind of attention to what is said. As such a substitute, as well as a book of reference later, this book is well adapted, and we hope that it will come into the hands of many students.

The translation has, obviously, been made with much care. Some hours of turning the pages have discovered no mistranslations more serious than optional for arbitrary; vaporization for boiling; and anthracite for bituminous. "Boron occurs only trivalent," and "simpler constructed," are samples of the worst of the not too numerous faults of style. It is chiefly in the connections between two sentences or parts of sentences, in the use of but, or however, or on the contrary, that translation betrays itself. This is by no means faint praise; the translator is to be congratulated on having successfully and well completed his task.

Errors of fact are few. The temperature at which water has a density the same as at zero is made 9° instead of 8°; the density of ice at zero is made 0.93, which is a survival. Such trifles are inevitable, and that there are no more is high praise. But there is one respect in which the translator should revise the language of the original. Wherever ratios and proportions are mentioned, as in discussions about the atomic theory, or about densities and molecular weights, statements are made, some of which are erroneous and some vague and obscure; this, too, in regard to a subject where the utmost clearness and accuracy are none too much for the student. Page 13, "Only a definite quantity by weight * * * can take part, etc. This is too obscure a way of saying that the quantities of the two elements bear a definite ratio to each other. Page 11, "These proportions by weight * * * are always a whole multiple of the lowest quantity by weight, etc." A proportion or ratio is made a multiple of a weight, and the phrase *integral* multiple excludes ferric oxide from the list of compounds. Page 26, ammonia "has the specific gravity 17.07 with respect to oxygen taken as unity"; and in other sentences the molecular weight of oxygen is said to be the unit of molecular weights. It is, of course, intended that the molecular weight of oxygen is the *basis* and that one-sixteenth of the molecular weight of oxygen is the *unit* of molecular weights. It is to be hoped that a second edition will soon give opportunity to revise statements of the kind described.

The printer has done his work well. The page is attractive, the type clear and the paper satisfactory.

EDWARD W. MORLEY.

TRAITÉ D'ANALYSE DES SUBSTANCES MINÉRALES, PAR ADOLPHE CARNOT. Tome second. Metalloïdes. Paris: V^ve^ Ch. Dunod, Éditeur. 1904. 821 pp.

The first volume of this work, which appeared in 1898, was devoted to an unusually detailed discussion of the methods of quali-

tative chemical analysis and of those types of procedure in quantitative analysis which are of general application. The present volume deals with the specific methods of determination of the metalloids under which the author includes hydrogen, oxygen, nitrogen in its various compounds, the argon group, carbon, its oxides and other important compounds, the halogens, sulphur, selenium, tellurium, phosphorus, arsenic, boron, silicon, titanium, tantalum, niobium, tungsten, molybdenum and vanadium. For each of these elements, and for most of the compounds, there is also given a statement regarding the occurrence in nature, the methods of qualitative detection and, in the case of the elements, the properties of the principal compounds, especially of the oxides.

The value of a treatise upon analytical chemistry of the magnitude of the present work should lie largely in the assistance which it affords the analyst in the selection of reliable methods from the bewildering variety presented in the manuals and journals, as well as in the readiness with which it directs the reader to original sources of information. Of the importance to chemical literature of Professor Carnot's work there can be no question, and the present volume presumably represents his preferences with respect to methods which, as the result of his experience, are surely entitled to respect. One can hardly escape the impression, however, that there is an over-preponderance of French authorities among those cited, or avoid the wish that the author had been willing to discuss the procedures somewhat more critically, and that, instead of giving only the name of the investigator to whom special procedures are to be ascribed, specific references to journals or manuals had been more frequently given. The omission of any authority for the table of densities and contents of sulphuric acid (page 447), or any statement as to whether the gravities are referred to water at 4° or 15° is surely unfortunate. Cross references throughout the volume itself would also add much to its usefulness. For example, one finds on page 421 a procedure for the determination of sulphur in pyrite by an oxidation method, but the difficulties encountered in the precipitation of barium sulphate in the presence of iron are not discussed until page 453 is reached and then under the heading "Soluble Sulphates." The work of Lunge is there referred to only briefly, and one is surprised to find no reference to that of Küster and Thiel. Indeed, no application of the ionic hypothesis appears to have been made throughout the volume.

But the impressions of painstaking thoroughness and evident mastery of his subject, displayed by Professor Carnot, in the first volume of this treatise are also evident in this, its successor, especially in the wide range of procedures presented and their applications to minerals and mineral products. Both volumes constitute valuable additions to our authoritative reference books and it is to be hoped that the author will find the time and strength to complete the third volume in the near future. H. P. TALBOT.

DIE CHEMIE DER ZUCKERARTEN. DRITTE VÖLLIG UMGEARBEITETE AUFLAGE. VON PROF. DR. EDMUND O. VON LIPPMANN, Direktor der Zuckerraffinerie Halle zu Halle. Braunschweig: Friedrich Vieweg und Sohn. 1904. Price, bound, 34 marks.

The third edition of this standard work appears in two volumes, numbering in all about 2,000 pages, which is nearly twice the size of the older work of 1895. Comparing the two editions one is impressed with the large amount of new material which has been added to our knowledge of sugars during the past decade. The work of revision and enlargement has been most thoroughly accomplished, bringing the work completely abreast of the times.

The author has accorded the chemistry of the different sugars his usual exhaustive treatment, approaching the subject from all standpoints—the general, analytical, physical, biological and industrial. The work will, therefore, possess an interest, not only for the specialist in sugar chemistry, but also for those engaged in other fields. The food chemist, the mycologist and bacteriologist, the agricultural chemist, and those interested in the technical sides of the sugar and fermentation industries will find the work invaluable.

The general method of treatment, laid down in the previous editions, has been followed throughout, the author holding fast to the principle of making the book purely a treatise on sugars, giving only such attention to allied compounds and derivatives as may be necessary to a thorough understanding of the subject. While this plan of treatment is not so comprehensive as that adopted in some other works, such as Tollens' "Handbuch der Kohlenhydrate" and Maquenne's "Les Sucres," where the various alcohol and acid derivatives of the sugars are given individual attention, the limitation is nevertheless a wise one. In a work of such special character the boundary lines must necessarily be closely drawn.

The first volume of the new book is devoted entirely to the monosaccharides, beginning with the dioses and passing up the

scale to the sugars of higher molecular weight. In the second volume the compound sugars are taken up—the di-, tri- and tetrasaccharides. The higher polysaccharides, starch, cellulose, etc., are placed outside the class of sugars and are, therefore, not given special attention.

Nearly 400 pages of the second volume are devoted to cane-sugar, and this part of the work alone is the most comprehensive treatise upon the chemistry of sucrose yet compiled. The opinion of von Lippmann, in regard to the much-debated question concerning the influence of temperature upon the specific rotation of sucrose is of particular interest. While criticizing, in part, the work of Wiley along this line[1] he is not at all prepared to accept the conclusion of Wiechmann that the influence of temperature is to be wholly disregarded.

In the concluding part of Volume II a number of chapters are devoted to the chemistry of sugars in general. The main facts concerning the constitution, configuration and synthesis of the various sugars are presented; the relations between the optical, colorimetric and other physical constants are also discussed. The various theories regarding the origin and formation of the sugars in the plant are fully presented, likewise the nutritive value of the different sugars and their physiological rôle in the animal organism.

Forty pages of addenda, consisting of abstracts made while the volumes were in press, bring the work completely up-to-date. A very satisfactory index, both of authorities and subject-matter, is given at the end of the second volume.

In the matter of nomenclature von Lippmann, as in previous editions, adheres to the old system advocated by Scheibler—a policy which is no doubt open to considerable criticism. The author, however, does not believe the time to be ripe for the more scientific and rational nomenclature of the sugars, advanced by Fischer. His objection to the term *glucose* and preferment for *glycose* upon purely etymological grounds are surprising when we note his own defiance of all etymological rules in substituting for *furfural* the new term *furol*. It is agreeable to note, however, that the author does not belong to that school of recent reformers who begin cellulose, cellose, etc., with z.

[1] This Journal, **21**, 568.

As a reference work upon all that pertains to the chemistry of sugars, von Lippmann's "Chemie der Zuckerarten," already a classic, will occupy for many years a leading place.

C. A. BROWNE, JR.

THE OCCURRENCE OF ALUMINIUM IN VEGETABLE PRODUCTS, ANIMAL PRODUCTS, AND NATURAL WATERS. By C. F. LANGWORTHY, PH.D., and PETER T. AUSTEN, PH.D. New York: John Wiley and Sons. 168 pp. Price, $2.00.

In this book is found a citation of all known references to the occurrence of aluminum in food products and natural waters. The work is not to be considered as a complete bibliography of aluminum, since it deals only with the occurrence of this element in vegetable and animal products, natural waters and a few miscellaneous materials such as edible earths. The authors do not make any comment on the value of individual analyses, nor do they comment upon the probable effect of the quantity of aluminum salts found in the bodies mentioned upon the health.

The material is arranged alphabetically according to authors names. This arrangement would detract very much from the value of the book as a reference manual were it not for the very complete index which accompanies the text. This index extends over 36 pages and renders the finding of the occurrence of aluminum salt in any of the products mentioned, easy.

Part I of the book, pages 1 to 48 inclusive, treats of the occurrence of aluminum in vegetable products; Part II, pages 49 to 50 inclusive, in animal products; Part III, pages 51 to 130 inclusive, in natural waters; and Part IV, pages 131 and 132, in miscellaneous materials.

Many observers have reported aluminum as a natural constituent in the ash of cereals used in bread-making. For instance, Yoshida, on page 45, states that the ash of wheat contains 0.106 per cent. alumina, of buckwheat 0.113, barley 0.140 and rice 0.189. On page 45 it is also stated, on the authority of W. Blythe, that all bread contains more or less alumina.

According to Teller, pages 36 and 37, the presence of alumina in the ash of wheat and its milling products depends largely upon the character of the soil. Considerable quantities of aluminum oxide were found in the ash of wheat and its milling products when the wheat was grown in Arkansas, while a sample of wheat grown on a sandy plot in Michigan was found to be free of alumina.

The attempt lately made to use salts of alumina for preserving meat renders it of interest to know whether or not meat naturally contains this product. The information on this subject contained in the book is necessarily very meager. Aluminum has been found in the ash of milk where it exists in conjunction with oxide of iron.

It is stated on page 50 that a trace of alumina has been found in veal and in the ash of beef. Fifteen per cent. of the ash of egg albumin is stated by one author to consist of phosphate of alumina. The large quantity of alumina found in bat excrement, noted on page 50, may be wrongly interpreted as it stands. The excrement in question, as will be seen by consulting the *American Chemist* cited, contained a quantity of material which is stated by McMurtrie to be an accumulation of silicious clay. It is probable, therefore, that the greater part of the alumina, reported in this excrement, came from the earth and not from the bats. It is to be regretted that the data relative to the natural occurrence of alumina in edible meats are so meagre in chemical literature.

The occurrence of alumina in natural waters is not a matter of surprise and the data in regard to this are very full and complete.

The book will be found of interest, especially to analytical and physiological chemists and health officers.

It is evident from an inspection of the data in the book that the occurrence of traces of alumina in certain food products may often be expected.

H. W. WILEY.

THE ELEMENTS OF PHYSICS. VOL. I.: MECHANICS AND HEAT. By EDWARD L. NICHOLS and WILLIAM S. FRANKLIN. Third edition, rewritten, with additions. New York: The Macmillan Co. x + 290 pp. Price, $1.90 net.

As the earlier editions of this work have been previously reviewed in this Journal (**25**, 113), little more is necessary than to call attention to the appearance of the new edition, and to the facts that several important chapters have been rewritten, that a new one on the Transfer of Heat has been included, and that a valuable set of 66 problems has been added. The work is characterized by great conciseness of statement, by the definition of a vast number of physical concepts, and by the formal statement of many principles, which are discussed briefly and abstractly, and are mathematically formulated and demonstrated wherever this is possible. The work seems adapted far more to the advanced student of physics, who might desire to review and make more precise his conceptions of the subject, than to the ordinary college student.

A. A. NOYES.